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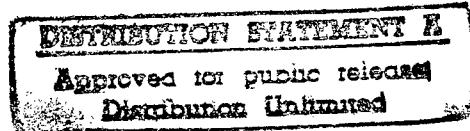
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and Exhibition on Advanced Materials Technology]

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PAN-Based Carbon Fibers

[Article by Toru Hiramatsu, head, Torayca Laboratories Composite Materials Research Center, Toray Co., Ltd.]

[Text] 1. Introduction

As is evident from Figure 1, carbon fibers (CF) have high values for specific strength and specific modulus of elasticity as compared to other reinforcing materials. For this reason, they are widely employed as advanced composite materials (ACM). More than 95 percent of the CF used as structural materials are PAN-based CF. This is because of their balanced composite characteristics and superior workability.

2. General Outline of PAN-Based CF

The demand for PAN-based CF has rapidly increased in the 20 years since their first industrial production around 1970. Today (1990), the world's consumption of PAN-based CF tops 6,800 tons. A breakdown of this consumption is shown in Table 1. It can be seen that space/aeronautical and sports/ leisure applications each account for about 40 percent. Japan is responsible for about half of the world's production of PAN-based CF, as shown in Table 2. As shown in Table 3 (CF applications), there is now a diversified range of applications that take advantage of the physical, chemical, and superior mechanical characteristics of CF, such as its stable dimensions, chemical resistivity, and superior heat and electrical conductivity.
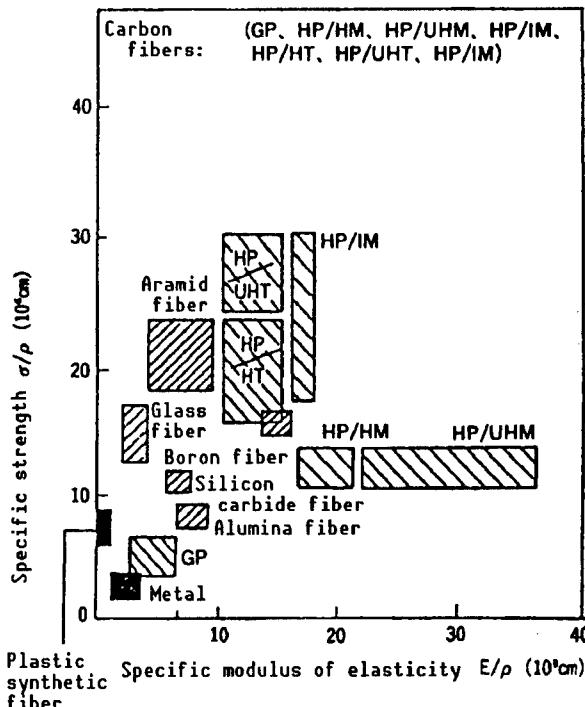

Figure 1. Specific Strengths and Specific Moduli of Elasticity of Various Materials

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Table 1. PAN—Based CF Consumption in 1990

(Units: Tons)

	Airplanes/ space vehicles	Sports/ leisure	Industries	Total
United States	2,000 (65)	500 (16)	600 (19)	3,100 (100)
Europe	670 (58)	200 (18)	280 (24)	1,150 (100)
Japan	50 (4)	780 (62)	420 (34)	1,250 (100)
Others	40 (3)	1,160 (93)	50 (4)	1,250 (100)
Grand total	2,760 (41)	2,640 (39)	1,350 (20)	6,750 (100)

Table 2. Production Capability for PAN—Based CF

(Units: Tons/year)

Name of company	Production capability	Scheduled pro- duction increase
Asia Toray Toray Rayon Mitsubishi Rayon Shin Asahi Kasei Kaabon (New Asahi Chemical Carbon) Taiwan Plastics	2,250 2,020 500 450 230	+500/93
United States Hercules Amoco BSM Courtaulds Akzo Zoltek BPAC	1,750 1,000 450 360 360 110 40	+900/91
Europe Courtaulds Akzo Soficar R.K. Carbon	350 350 340 230	+360/92
Grand total	10,790	+1,760

(Note: As of November 1990

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Table 3. Characteristics and Applications for Carbon Fibers

Mechanical properties (strength/modulus of elasticity)	Space/aeronautics, sports/leisure, material for general structures
Dimensional stability	Space instruments, radio telescopes, precision instruments (molds, drawing instruments, etc.
Fatigue resistivity	Helicopter blades, etc.
Vibration attenuation property	Audio equipment, etc.
Heat resistivity	Insulators, rocket nozzle cones, brakes in airships, etc.
Chemical resistivity	Packing, filters, etc.
Electrical properties	As materials in various electrodes, in shields for electromagnetic waves, in antielectrostatic materials, etc.
Biocompatibility	Artificial bones, tendons, etc.
X-ray transparency	X-ray equipment
Others	Activated carbon fibers

PAN–based CF are produced using the process shown in Figure 2 from an acrylic fiber precursor made of spun polyacrylonitrile (PAN). The changes in its chemical composition during oxidation and carbonization reactions are shown in Figure 3. A model structure of PAN–based CF is depicted in Figure 4. Microcrystals formed into sheet layers of graphite mesh are arranged along the fiber axis. In addition, the carbon fiber can be classified into carbon and graphite fibers depending on maximum temperature during thermal treatment. Graphite fibers have better developed microcrystals, and, in general, less strength but a higher modulus of elasticity.
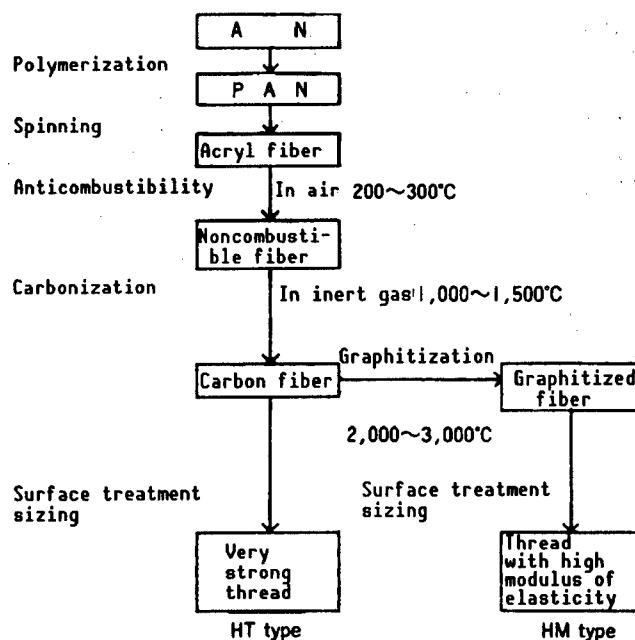
Figure 2. PAN–Based CF Production Process

3. R&D Trends in PAN-Based CF

In recent years, the most significant advances in technology have been achieved in the development of very strong and ductile CF for use as materials in the primary structures of airplanes, and the development of very strong and elastic CF for use in lightweight and high performance fishing rods and golf club shafts.

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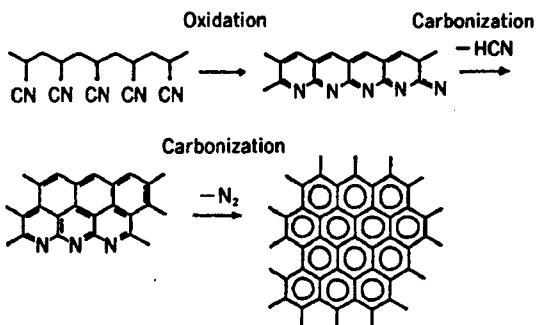
Figure 3. Structuring of PAN–Based CF
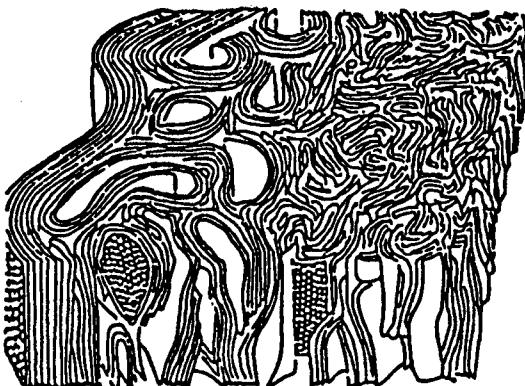
Figure 4. Model Structure of PAN–Based Carbon Fiber

3.1 Development of Very Strong and Ductile CF

Table 4 compares the theoretical and experimental values for the strength and modulus of elasticity of CF. The experimental value for the modulus of elasticity is about 80 percent of the theoretical value.

Table 4. Experimental and Theoretical Values for Strengths and Coefficient of Elasticity for CF

Item		Unit	Graphite	Polyethylene
Theoretical value	Strength	GPa	180	32
	Coefficient of elasticity	GPa	1,020	240
Experimental value	Strength	GPa	Whisker 20 PAN–based CF 7	Gel spun fiber thread 4 Dissolution and spun thread fiber 1
	Coefficient of elasticity	GPa	Pitch–based CF 830 PAN–based 590	Gel spun fiber thread 170 Dissolution and spun thread fiber 10

Meanwhile, its strength is only about 5 percent of the theoretical value. This difference between the experimental and theoretical values for the modulus of elasticity is due to the basic CF structure, such as the degree of crystallization, orientation, etc. The difference in the case of strength is due not only to the basic structure, but also depends on the presence of defects like

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voids, surface imperfections, adhesive particles, impurities, etc. In reality, it has been demonstrated through scanning electron microscope (SEM) photographs of fractured cross sections of CF, as shown in Figure 5, that defects originate from fractures. The dimension and strength of the defect (point of origin of fractures) has the correlation depicted in Figure 6. The smaller the size of the defect in the form of voids, the stronger the CF is. By reducing the effects of defects, a material with a strength of 3.5 GPa (360 kgf/mm^2) and a ductility of about 1.5 percent was developed in the early 1980s. Today, a far superior product in the form of PAN-based CF with a strength of 7 GPa (720 kgf/mm^2) and a ductility of 2.4 percent is available.

3.2 Development of CF With a High Modulus of Elasticity

The modulus of elasticity of CF and its basic structure, including the dimensions of its microcrystals and their degree of orientation, were proved to have the correlation depicted in Figure 7. The CF material with a modulus of elasticity of 390 GPa (40 tf/mm^2) that was available in the early half of the 1980s has been greatly improved to one with a modulus of 640 GPa (65 tf/mm^2) in the form of PAN-based CF.

3.3 Development of Very Strong and Highly Elastic CF

The difficult to graphatize PAN-based CF has a lower modulus of elasticity when compared to the easier to graphitize pitch CF. In reality, pitch CF sells better despite the fact that its fracture ductility and composite compressibility is lower, and it has inferior workability. PAN-based CF also encounters the same kind of problems, to a varying degree, when its modulus of elasticity is improved. Very strong, highly elastic CF was developed, therefore, through a combination of techniques to improve its strength, elasticity, and ductility. Very strong CF with a high modulus of elasticity possess not only a higher fracture ductility when compared to conventional highly elastic CF, but also enjoy improved composite compressibility, as shown in Figure 8.
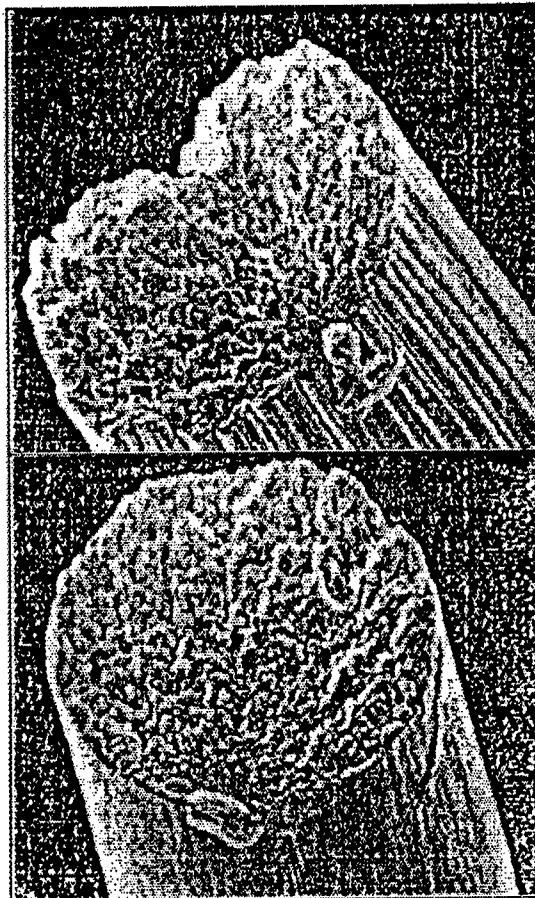
Figure 5. Defects in Fracture Cross Section
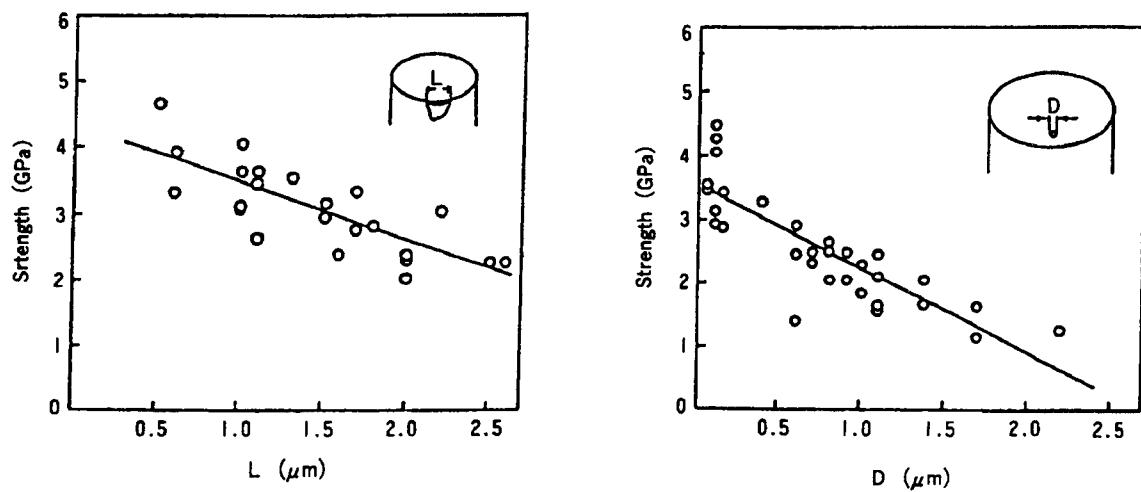
Figure 6. Dimensions and Strengths of Defects
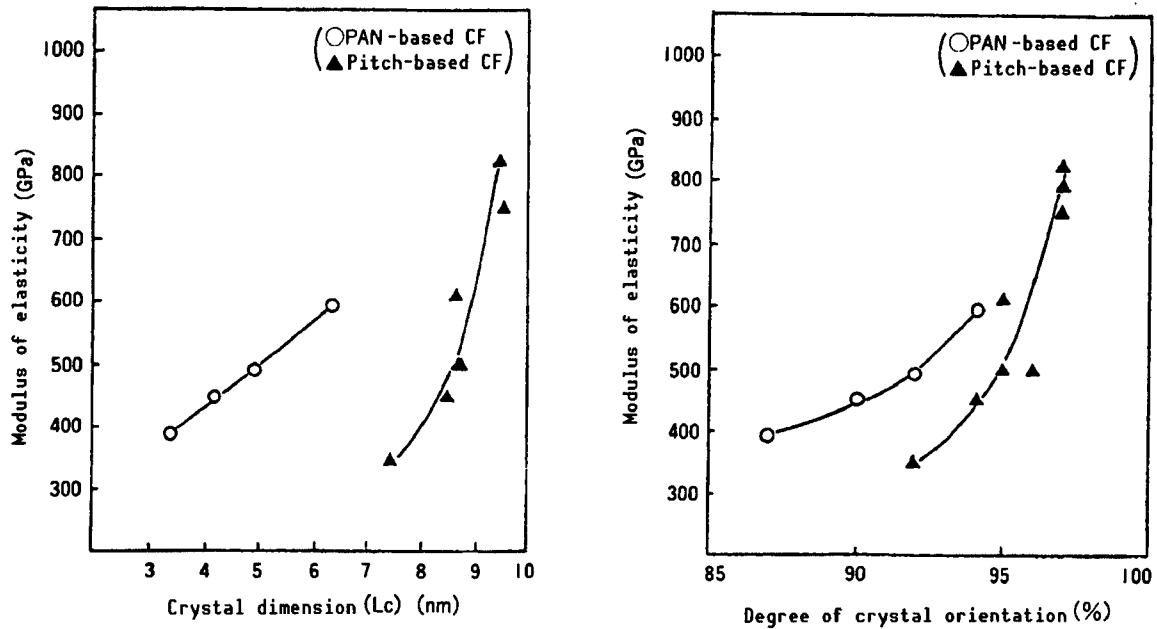
Figure 7. Basic Structure and Modulus of Elasticity of CF

4. Conclusion

An extremely large number of PAN-based CF that have been improved through technical breakthroughs in the past several years and whose strength and modulus of elasticity are depicted in Figure 9, is now available for market expansion. In conclusion, the use of high performance PAN-based CF as primary structural materials in large passenger aircraft will be described. Normally, PAN-based CF are limited to secondary structures like ailerons and such.
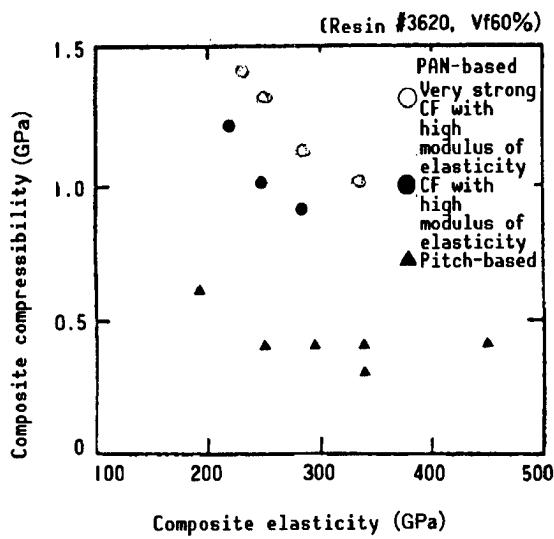
Figure 8. Composite Compressibility
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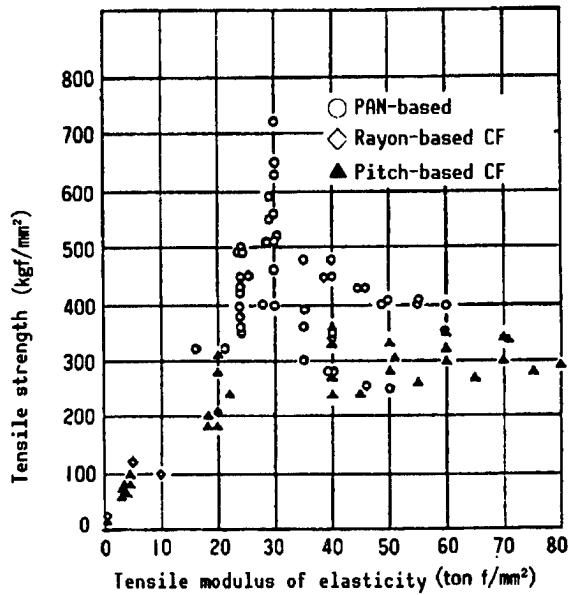
Figure 9. Mechanical Characteristics
of Commercially Marketed Carbon
Fibers
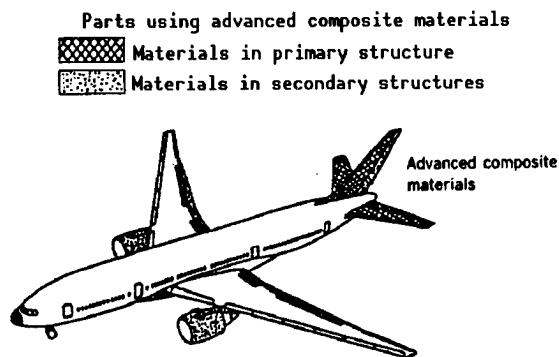
Figure 10. Parts of Boeing 777 Using
CFRP

Carbon fiber—reinforced polyimide (CFRP)
constitutes only about a mere 3 percent
of the total body weight of the air-
craft. This figure will be raised to 20
percent in future aircraft like the
Boeing 777 whose maiden flight is sched-
uled for 1995. As shown in Figure 10,
the tail wing and primary structures of
the Boeing 777 will be made of PAN—based
CF. There are great expectations for the
application of CF and matrix resins with
improved performance in the main wings
and body of future aircraft.

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1.   INDUSTRIAL MATERIALS, Vol 38 No 18, 1990, p 34.

2.   Matsui, JOURNAL ON PRECISION ENGINEERING, Vol 56 No 4, 1990, p 622.

3.   Saito and Ogawa, INDUSTRIAL MATERIALS, Vol 33 No 8, 1985, p 103.

4.   Hiramatsu, PLASTICS AGE, June 1988 issue, p 115.

New High-Performance, Pitch-Based Carbon Fibers

[Article by Kimitaka Sato and Norio Tomioka, Advanced Technology Research Center, Nippon Steel Corp.]

[Text] Pitch-based carbon fibers (CF) possess characteristics that are far superior to many competitive fibers. In particular, the high-performance, very strong pitch-based carbon fiber is still in its infant stage, and future developments are expected.

The basic technology for pitch-based CF was developed by Otani.[1,2] Meanwhile, Kureha Chemical Japan and Amoco Performance Products (United States) have long been known for the manufacture and commercial marketing of short and long fibers, respectively. In recent years, particularly in Japan, there has been a renewed interest in pitch-based CF. Active research efforts[3-13] to improve the performance and strength of these CF are some of the activities that should be mentioned. This renewed interest could be attributed to policies in 1) the effective deployment of resources (pitch starting material), and 2) management diversification (to gain a foothold in the field of new materials). Recently a certain trend can be observed among companies that are narrowing the focus of their research. This probably is due to "an understanding of the technical priority and difference" or an "understanding of the existence of a market worth the high research investment."

In such an environment, the following trends can be observed among corporations that are relatively active in research in pitch-based CF:

a. Pitch starting material: Mitsubishi Gas Chemical (synthetic pitch)
  Mitsubishi Sekiyu (synthetic pitch)
  Maruzen Petrochemical (carbon pitch)

b. Carbon pitch: Donac (production capacity: 300 t/year)

c. Petroleum pitch:
  Long fibers: Nippon Oil Group (production: 50 t/year)
  Token (production: 12 t/year)
  Short fibers: Ashland Chemical (production: 200 t/year)

Japanese companies have focused their attention on the high performance of long fibers, and it is not by chance that all of them have a research history of about 10 years. It goes without saying that these companies have accumulated an extremely high level of expertise. For instance, Japan has already established production procedures for very strong, high-performance products with tensile strengths of ~350 kgf/mm² ("Eskainos" from Nippon Steel, "Granoc" from Nippon Oil, etc.) as compared with the predecessor, Amoco's "Thornel" P-75S (tensile strength ~225 kgf/mm²). Also, new applications for the new Japanese products are steadily being charted.

In this article, we will introduce the high-performance pitch-based carbon fibers that are the product of the expertise and knowledge accumulated over the years by each of the above-mentioned companies, the production methods and characteristics of the fibers, developments in applications for those advanced composite materials, and will touch on current technical problems as well as future expectations.

1. Fiber Production Method and Characteristics

(1) Production Method and Strengthening of Fiber

The pitch starting materials for use in pitch-based carbon fibers can be divided into optically isotropic and anisotropic (mesophase) types. Both are spinnable pitch reformed and refined from heavy oil like catalytically cracked residual oil from coal tar or petroleum. An example of the characteristics of this pitch starting material is shown in Table 1.

Table 1. Examples of Characteristics of Refined Pitch as Starting Materials of Carbon Fiber

	Petro-leum pitch A	Petro-leum pitch A	Petro-leum pitch B	Petro-leum pitch C	Petro-leum pitch A	Petro-leum pitch B
a. Softening point (°C)	250	304	308	299	257	265
b. Ti (%)	58	81	86	95	43	74
c. C (%)	93.9	94.9	94.2	95.2	94.4	95.3
d. N (%)	0.2	0.68	1.05	0.89	<0.1	<0.1
e. S (%)	0.7	0.16	0.28	0.15	<0.01	0.16
f. H/C	0.59	0.47	0.50	0.48	0.75	0.63

In the pitch-based carbon fiber production process, this refined pitch starting material is melt spun into pitch fiber, changed into carbon fiber through infusion and carbonization, and then finally into graphite fiber through a graphitization process. Optically isotropic pitch becomes general-purpose carbon fiber, while the anisotropic type becomes high-performance carbon fiber through a spinning process. These carbon fibers possess different fiber characteristics.

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Pitch-based carbon fibers are the result of a combination of different technologies in such fields as chemical reactions, spinning, high-temperature furnaces etc. The following is a summary of the technical breakthroughs that were vital to the strengthening and improving the performance of the fiber:

    a. Production of high-performance pitch with no defects during spinning.

    b. Graphite fiber crystal structure control through control of the crystal structure during spinning.

    c. Control of crystal orientation and fiber characteristics through control of the infusion level.

(2) Fiber Structure and Characteristics

The crystal structure of carbon fibers is similar to that of graphite, as shown in Figure 1. Many benzene ring planes are arranged along the fiber axis, and these planes are layered with a distance of d_{002} between them.[14] The more advanced graphitization is (in other words, the higher the values for tensile elasticity), the smaller the distance between the planes (interplanar distance, d_{002}) until it reaches the ideal value of 0.335 nm for graphite. This layered structure is, in reality, not arranged neatly in order but is either bent, broken or even not in line with the fiber axis. An example of a model of the microstructure of a carbon fiber is shown in Figure 2.[13] It has been proven that each structure factor is very different from that of conventional pitch-based or even PAN-based carbon fibers.

Figure 3 compares the tendencies of tensile characteristics of pitch- and PAN-based carbon fibers, and the current figures for some pitch-based CF are shown in Figure 4.[11]

Figure 1. Approximate Orientation of Crystal Structure for Carbon Fiber (D.D. Edie[14])
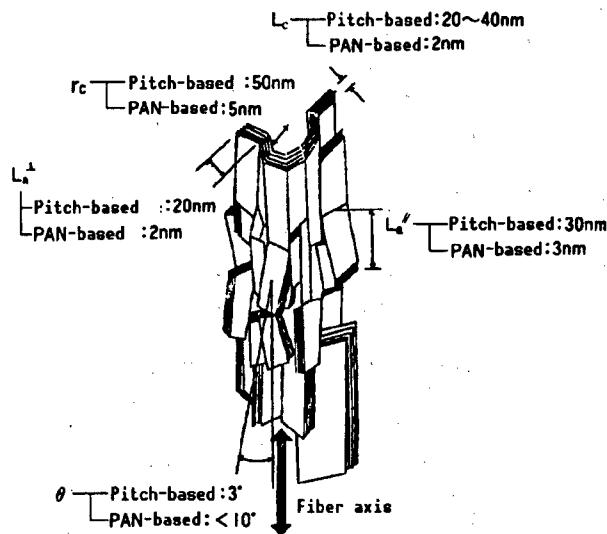
Figure 2. Microstructural Model of Carbon Fiber (by Nippon Steel's researchers[13])

The theoretical tensile strength[15] along the direction of the network plane of the graphite crystal is ~18 tf/mm^2.[15] Although a carbon fiber is a very structure-sensitive material, its tensile strength is strongly influenced by macro defects. As such, the PAN-based type[16] is estimated to have a

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characteristic fiber strength of 900-- 1000 kgf/mm^2, while that of the pitch- based type[17] is ~700 kgf/mm^2. The ten- sile strength of PAN-based CF was ~230 kgf/mm^2 about 20 years ago.[18] Compared to that, the pitch-based type has al- ready attained ~350 kgf/mm^2, an indica- tion that there is still lots of room for progress in the future. Japan leads the world in technologies for strength- ening and improving the performance of pitch-based carbon fibers. For example, it is believed that the development of a fiber with a tensile strength of 500 kgf/mm^2, a tensile elasticity of 50 tf/mm^2 and an elongation of 1 percent will be realized in the very near fu- ture.

O、 △:Coal tar pitch-based (Nippon Steel "Eskainos")

▲   :Petroleum pitch-based (Amoco "Thornel")

●、 ●:PAN-based (Toray "Torayca")
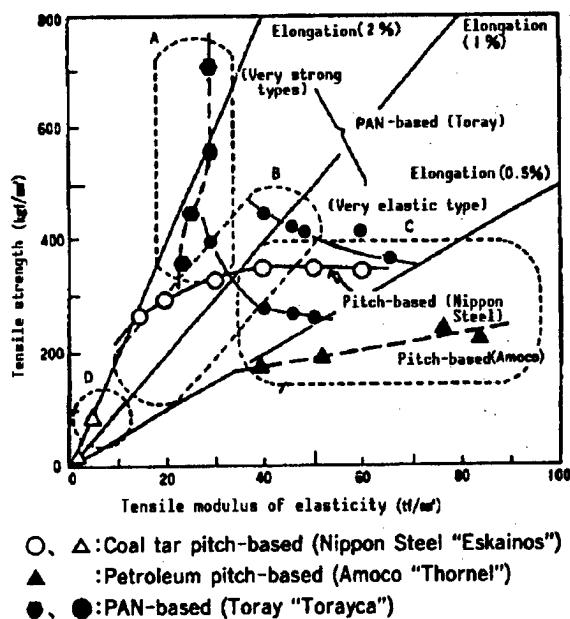
Figure 3. Tendency of Tensile Characteristics of Pitch-Based and PAN-Based Carbon Fibers

A. Nippon Steel "Eskainos" (coal tar pitch-based)

B. Mitsubishi Kasei "Dialead" (coal tar pitch-based)

C. Nippon Oil "Granoc" (petroleum pitch-based)

D. Amoco Performance Products "Thornel" (petroleum pitch based).
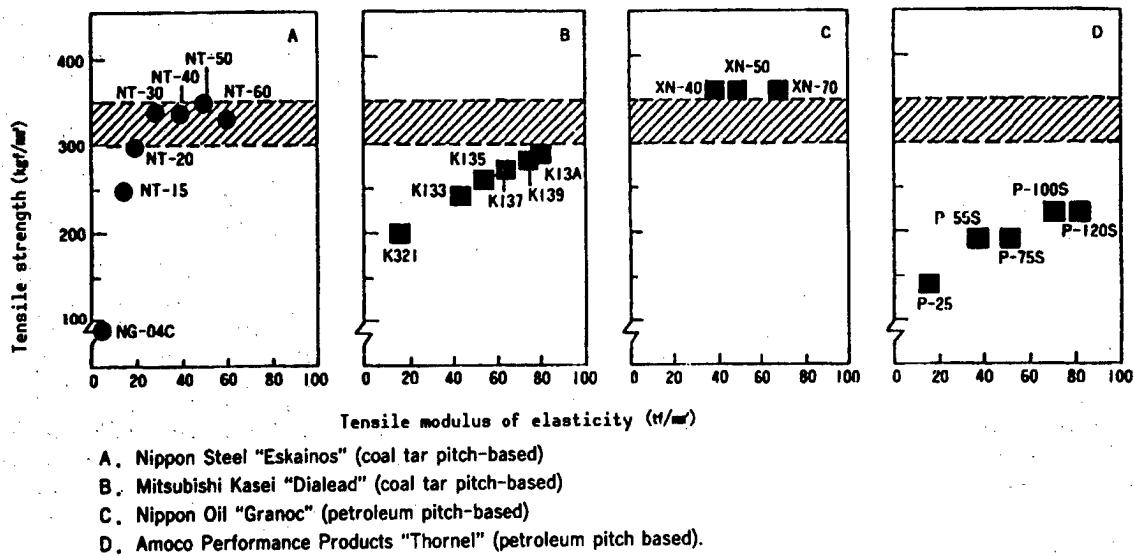
Figure 4. Tensile Characteristics of Some Pitch-Based Carbon Fibers
(K. Sato[11])

(3) Distinguishing Applications Suitable for PAN-Based and Pitch-Based Carbon Fibers

Pitch-based carbon fibers are similar to PAN-based carbon fibers in terms of technology, the physical properties of the fiber, and applications, but there also are innumerable differences and thus these two materials should not be

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Table 2. Comparison of Characteristics of Pitch-Based and PAN-Based Carbon Fibers

|	Pitch-based carbon fiber	PAN-based carbon fiber
a. Tensile strength	•Relatively low (~350 kgf/mm²)	•High (360~370 kgf/mm²)
b. Tensile modulus of elasticity	•Material with high modulus easily made at relatively low temperature treatment (0.5~80 tf/mm²)	•Relatively low, high temperature required for making high modulus (24~40 tf/mm²; >50 tf/mm² is special grade)
c. Fiber radius	•Slightly thick (9~10 μmφ)	•Thin (5~7 μmφ)
d. Density	•Relatively high (~2.0 g/cm²)	•Relatively low (~1.8 c/cm²)
e. No. of filaments	•500~4,000/strands (Some may be threaded)	•1,000~12,000/strands (special grade as >12 K)

considered the same. The characteristics of pitch-based carbon fibers are compared to those of PAN-based fibers in Table 2. Pitch-based fibers have many differences not only in their mechanical properties, but also possess interesting tendencies in terms of density, heat and electrical conductivity, resistance to oxidation,[4] etc.

For example, the fiber density varies according to the type of starting material,[19] as shown in Figure 5. In other words, the fiber density approaches 2.26 g/cm³, the ideal value for graphite as the tensile modulus of elasticity of the pitch-based fiber increases. On the other hand, the fiber density for PAN-based carbon fibers remains at a relatively low level even when its modulus of elasticity has a high value of 50~60 tf/mm².

Figure 5. Density Characteristics of Carbon Fibers According to Various Kinds of Raw Materials

However, a number of competitors have appeared during a time when there has been technical progress in both pitch- and PAN-based carbon fibers. For example, PAN-based carbon fibers used to be manufactured with tensile moduli of elasticities ranging from 24~60 tf/mm². Recently, however, Toray Rayon and Toray have expanded this range by marketing "LM-16" (tensile strength 320 kgf/mm²; tensile modulus of elasticity 16 tf/mm²) and "M65J" (tensile strength 370 kgf/mm²; tensile modulus of elasticity 65 tf/mm²), respectively. Pitch- and PAN-based carbon fiber applications gradually will be distinctly delineated as product quality and characteristics, cost, and market needs arise.

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Table 3. Some Examples of Preferable Industrial Use for Carbon Fiber Reinforced Composite Materials

Structural material
  Industrial sector
    Social background
	Examples of forecast applications

Structural material a. Railway •Lightweight carriers that can withstand high speeds (Super Hikari, linear motor car, etc.)	•Carriage, streamlining of structure of front carriage, framework of carriages, supportive material for adiatabic heat load in superconducting magnets.
b. Automobile •Improved fuel consumption in accordance with CAFE (corporate average fuel economy) regulations. Recyclable and improved comfort.	•Body, engine, peripherals (propeller shaft, etc.).
c. Aircraft/spacecraft •Weight reduction for improving fuel consumption in private aircraft. Lightweight super heat-resistant structural material for use in Orient Express, Space Shuttle, etc.	•Secondary structural material, related to interior decoration parts. Replacement for aramide fiber/glass fiber. Can be applied to C/C composite, boron-carbon composite material.
d. Ships •Highly appraised as corrosion resistant, extremely strong, and durable composite material for oceanographic development. Active movements in development of high-speed ships (cargo-techno superliner) in place of trucks.	•Realization of airports, cities and sewage treatment plants above the sea. Structural materials for ships.
e. Construction •Material weight reduction and improved strength for cutting cost through shortening length of time for projects proceeding under special conditions like high places, underground, in the ocean, or with labor shortages. Functional material	•Extremely tall flexible structures, bridges, development of underground space for reserve energy storage, foundation reinforcement material (geo textile), etc. Employed as curtain walls, CFRP cables, lock bolts, etc.
f. Energy/nuclear energy •Cost reduction of fuel battery and improved durability. Improved specific strengths of material used in rotating body of centrifugal separator for uranium concentration. Reduction of heat and increasing reliability of light water reactor thus improving its stability technology.	•Porous carbon fiber for use as material in electrodes. Changing the rotator of centrifugal separator into CFRP. Application of C/C composite as a material in light water reactor.
g. Medical •Improved functions for biological replacement parts. Improved sensitivity and smaller diagnostic instruments.	•Introducing CFRP for artificial muscles, artificial bones, tendons, artificial teeth, etc. Use of CFRP in diagnostic instruments and nursing robots.
h. Leisure (sports) •Improved specific strength and coefficient of elasticity for improved functions (better sense of feeling). Protection of human body, increase life span.	•Fishing rods, golf clubs, tennis rackets, etc.

Table 4. Comparison of characteristics of CFRP plates by various kinds of pitch-based carbon fibers with by PAN-based one

		Nippon Steel			Nippon Oil			Tonen		Mitsubishi Kasei				Toray		
		NT-20	NT-50	NT-60	E4025 (XN-40)	E5025 (XN-50)	E7025 (XN-70)	FT500	FT700	K-134	K-135	K-137	K-139	Torayca T300	M40	M46J
	Filament No./Strand	3000			1000/2000			3000		—				6000		
CF physical properties	Tensile strength kgf/mm²	300	350	330	330	330	340	300	330	220	260	265	280	360	280	430
	Tensile modulus of elasticity 10⁴kgf/mm²	20	50	60	40	50	70	50	70	50	55	65	75	23.5	40.0	46.0
	Fracture elongation %	1.50	0.70	0.55	0.8	0.6	0.5	0.6	0.5	0.42	0.5	0.4	0.4	1.5	0.6	1.0
	Fiber radius μm	10.0	9.5	9.5	10	10	10	10	10					7	6.5	5
	Fiber content g/km	470	455	450	150/300	150/300	150/300	510	520							223
	Fiber density g/cm³	1.95	2.09	2.13	2.12	2.14	2.16	2.14	2.16	2.10	2.10	2.12	2.13	1.76	1.81	1.84
	Volume specific resistance $\mu\Omega\cdot$m	13	8	7	8	7	4	8	5					20	8	8
	0°coefficient of linear expansion 10⁻⁶k	-0.5	-1.5	-1.5	-1.2	-1.3	-1.4	-1.0	-1.5	-1.0			-1.2	-0.7	-1.2	
	0°heat conductivity J/cm·sk	0.1	1.5	1.5	1	1.5	2.1	1.5	3.6	0.7			1.1	0.06	0.8	
Composite physical characteristics	0°tensile strength kgf/mm² (contribution rate)	170	199	188	150	150	160	128	142	112	126	133	140	180	125	225
	Modulus of elasticity 10³kgf/mm² (contribution rate)	11.6	29.7	35.6	23	29	40	29.2	39.2	30	33	39	44	14.0	21.5	26.0
	Degree of fracture elongation %	1.47	0.67	0.53	0.6	0.5	0.4	0.40	0.40	0.34	0.34	0.33	0.30	1.3	0.6	0.9
	90°tensile strength kgf/mm²	6.6	4.7	4.4	4.0	3.5	2.5	5.4	4.81	3.7	3.1	2.9	3.1			
	Modulus of elasticity 10³kgf/mm²	0.8	0.64	0.62	0.8	0.8	0.7	0.62	0.58	0.7	0.7	0.7	0.6			
	Degree of fracture elongation %				0.6	0.6	0.4	0.92	0.88	0.5	0.44	0.41	0.45			
	0°bending strength kgf/mm²	150	88	82	90	80	60	82.8	66.5					170	120	145
	Modulus of elasticity 10³kgf/mm²	9.5	25.5	28.9	17	21	31	22.3	31.6					14.0	19.5	23.5
	Degree of fracture elongation %				0.6	0.5	0.4									
	90°bending strength kgf/mm²	9.5	6.7	6.5												
	Modulus of elasticity 10³kgf/mm²	770	600	600												
	Degree of fracture elongation %															
	0°compressive str. kgf/mm²	99	54	52.5	50	45	35	40.6	39.8	50	50	43	41	170	120	130
	Modulus of elasticity 10³kgf/mm²	10.0	28.5	33.5	20	25	40	22.3	35.4	25	28	34	40			
	Degree of fracture elongation %							0.23	0.12							
	ILLS (interlaminar shearing strength) kgf/mm² (ILLS)	9.0	9.0	9.0	7.8	7.0	6.0	7.9	7.8	7	7.7	7.7	4.9	10	.8	9

(Notes) The above data were excerpted from the following:
a. Nippon Steel (Eskainos) :catalog
b. Nippon Oil(Granoc):NISSEKI REVIEW 32(1990), NO.5, P.197
c. Tonen (Forca)   :catalog
d. Mitsubishi Kasei (Dialead):Dialead Typical Properties (RP-701-01-1/2).
d. Toray (Torayca):catalog. Compressive characteristics excerpted from
Proc. 34th Intern. SAMPE Sym. (1989), p. 2579.

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2. Developments in Advanced Composite Materials

(1) Material Change Movements in Industrial Sector

The so-called "material revolution" was aimed primarily at making the material lighter and at improving its performance. Today, applications are not limited only to the aeronautical/space or sport/leisure sectors. It is not an exaggeration to say that the railway, automobile, construction and other industrial sectors are now facing a transition stage in the types of materials used. This transition in material types is illustrated in Table 3.

(2) Characteristics of Composite Materials

Composite materials reinforced by pitch-based carbon fibers include CFRP, CFRTP for plastic matrix cement/ceramic (CFRC), carbon (C/C composite) or metals (CFRM). The starting materials for these products are paper, felt, strings, biaxial and triaxial cloth, three-dimensional cloth, metals, carbon fibers with a cover layer of resin, resin compounds, and resin prepregs. Active research has been conducted to develop structural or performance materials that retain the characteristics of pitch-based carbon fibers. The mechanical characteristics of several types of pitch- and PAN-based CFRP (flat sheets) are shown in Table 4 as an example of one of the characteris-

tics of composite materials. Even in the case of pitch-based, there is a detection rate of more than 90 percent. Some peculiarities also exist in the tensile strength, bending strength, and ILSS (interlaminar shearing strength), although large discrepancies among the various pitch-based materials were not observed. The factors governing the characteristics of CFRP[20] are:

    a. Quality, configuration, and surface treatment of reinforced material

    b. Type, composition, and nature of resin

    c. Composition, laminar direction, constitution of reinforced fiber

    d. Type and constitution of packing material

    e. Molding method and conditions

    f. Testing method and conditions

Figure 6. Comparison of Compressive Strength of Pitch-Based Carbon Fibers to PAN-Based Fibers

In particular, in the case of pitch-based carbon fibers, there are many limitations in the porous thread related to the design of the spinneret nozzle. Thus, there are discrepancies in the values for the spun yarn depicted in Table 4. It is believed that the spinning and threading techniques play a major role in the determination of these figures.

Compressive strengths have the tendencies shown in Figure 6. As is evident, the PAN-based type is superior to the pitch-based type. Values for pitch-based type were found to vary depending on the manufacturing company.[4-13]

Table 5. Some Applications of Pitch-Based Carbon Fibers in Industrial Fields

Structral material
  Industrial sector
    Examples of applications
	Company involved in development

Structural material
  a. Aircraft/spacecraft
    •Body and parts in space shuttle "HOPE"
  b. Construction
    •Reinforcements for earthquake proof chimneys
    •CFRP sidewalks
    •CFRP water gates
  c. Others
    •Long, lightweight rolls for industrial use
Functional material
  d. Leisure (sports)
    •Lightweight boat (hybrid cloth with ultrahigh polymer PE fiber)
    •Weight reduction and improved rigidity in single scull (racing ship) (14.5 kg→11.5 kg)
    •Golf club
    a) Harmotec Pro HM-70/J's metal
    b) Mizuno Pro Ti-110/-120, Mizuno Eksa HM-80
    •Lightweight frame bicycle
 	
    •Two-wheel vehicle brakes
    •Ski Stock
  e. Others
    •Speaker cone
    •Mirror cylinder in telescopes
	•Kawasaki Heavy Industries/Kawasaki Steel
	
	•Ohbayashi-gumi/Mitsubishi Chemical
	•Mitsubishi Chemical
	•Tohnen
	
	•Nippon Steel Group
	
	•Bridgestone sports/Mitsubishi Chemical
	
	•Mizuno/Mitsubishi Chemical
	
	•Yoshida Bicycle/Tohnen
	•Lateed Pro/Nihon Sekiyu Group
	
	•Nisshin Kogyo/Mitsubishi Chemical
	•G.S. Technology (U.S.)/Tohnen
	
	•Kenwood/Tohnen
	•Takahashi Seisakusho/Nihon Sekiyu Group

(3) Development of Advanced Composite Materials

The preceding generation of pitch-based carbon fibers in the American market was supplied at a rate of about 200 t/year, and was originally intended for military uses (CFRM, nose cones, etc.), in space, and for brake linings in commercial passenger airplanes or military planes. In the future, however,

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demand in the general industrial sector for this material for structures is expected to rise, given that highly elastic products are being made that have high performance levels at lower cost. In Japan, active moves already have been made to apply pitch-based carbon fibers in the transportation and construction sectors. Recent developments in applications for pitch-based carbon fibers are listed in Table 5. Until recently, the main sectors using this material were construction, and sport and leisure, but the sector that is expected to employ large quantities of this material in the near future is the Japanese-French Friendship Monument[21] to commemorate the 200th anniversary of the French Revolution (scheduled to be constructed in Awajishima Park, Hyogo Prefecture) and the bridge across the Straits of Gibraltar[22] (figures are not announced yet).

Table 6. Estimated Global Demand for Carbon Fibers by Geographical Region and Market Segment, 1988–1990 (Segal)

Segment	Year	North America	West Europe	Asia	Regional total
Aeronautical/space	1988	2,550	410	90	3,050
	1993	3,730	860	225	4,815
	1998	5,860	1,640	370	7,870
Sport/leisure	1988	410	320	1,140	1,870
	1993	545	455	1,365	2,365
	1998	730	590	1,725	3,045
General industries	1988	270	230	770	1,270
	1993	545	365	1,275	2,185
	1998	1,090	500	2,045	3,635
Regional total	1988	3,230	960	2,000	6,190
	1993	4,820	1,680	2,865	9,365
	1998	7,680	2,730	4,140	14,550

Notes: a. Figures for 1988 are actual, units are in metric tons.
b. In the original article, West Europe region (1988) was 950 t. Figure changed to 960 t in this article.

3. Future Expectations and Problems

As described above, pitch-based carbon fibers are superior to other competing materials like PAN-based carbon fibers, glass fibers, aramid fibers, etc. According to the demand forecast published by Segal[23] shown in Table 6, demand in the aeronautical and space fields will be unchanged, while the sports and leisure sector will shrink. Meanwhile, demand in the general industrial sector

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will expand. Demand in Asia and North America is expected to grow. It is expected that by 1998 demand will reach about 15,000 tons.

(1) New Technical Challenges

More technical efforts will be necessary to improve the characteristics and to establish the position of pitch-based carbon fibers. The following break-throughs are notable points:

a. Improvement of the physical characteristics of the fibers, such as tensile strength and compressive strength. For that, control of the crystal's microstructure including crystal size, orientation, graini-ness, defects, etc., would be necessary.

b. Direct composite molding through near-net shape. The ultimate shape of a fiber-reinforced composite material is the near-net shape rather than the three-dimensional multiaxial one, as proven by tests. When composite with a matrix, the final product should be a continuous single body.[12-24,26] Further, it is vital for basic technologies like surface treatment and boundary techniques including sizing, to be established in the future, for the molding of composite materials.

c. Establishing material reliability.[26] A great number of factors affect the quality of the composite material during its processing. Thus, it is vital that techniques to analyze, assess, and standardize the product be established. Challenges have to be taken to develop trust and reliabili-ty in a product. A very important future theme to be tackled would be the collection of accurate data on fracture strains, breakability, fatigue, creep, strength against impacts, etc.

(2) Understanding the Market

As described above, pitch-based carbon fibers have many characteristics. Much effort, both technical and commercial, is required before it can establish a reputation.

a. Much time is required to develop applications for these fibers, whose tensile strength has reached a value of ~350 kgf/mm^2. The focus would be on the development of structural materials that take advantage of the high modulus of elasticity of the pitch-based carbon fiber.

b. An annual production of 300~1,000 tons would be the cost effective break even line, but before that can be achieved, it is important that a market worth this great amount of investment be developed.

The world of pitch-based carbon fibers is, to us, one "that allows significant progress in technology," one with a "magical attraction," and "with an eternal romance." Its development was not easy but if the developers were to pitch in their efforts to overcome the differences, in the near future, their efforts will definitely flower to become one of the leading materials of the 21st century.

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Advanced Materials for Extreme Environments

[Article by Akira Sakamoto, general manager, and Tomohiko Maruo, manager, Metallic Materials Technology, Next Generation Metals/Composite Materials R&D Association]

[Text] 1. Introduction

The space plane, the SSTS (supersonic transporter), and the HST (hypersonic transporter) in the aeronautical and space sector, like the coal gasification electric generator and nuclear fusion in the energy sector, are some of the projects that are planned for the beginning of the 21st century.
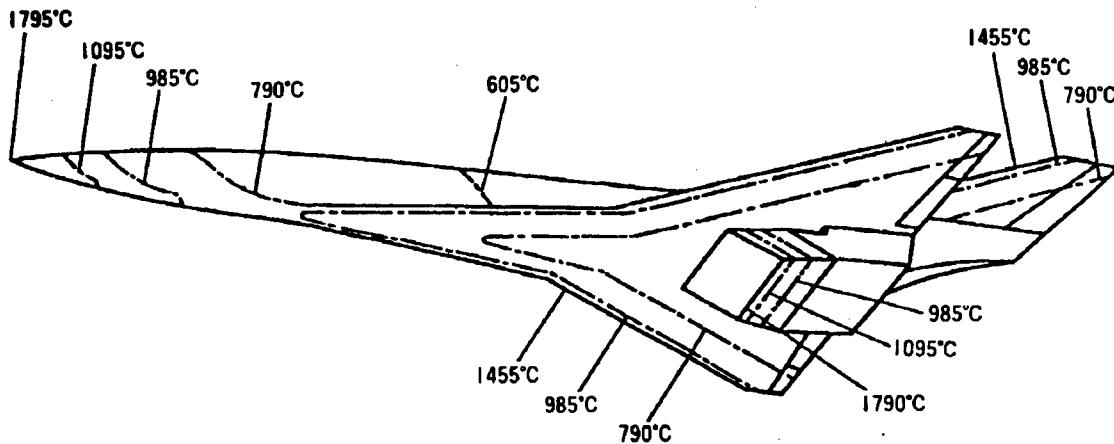
Figure 1. Example[1] of Body Surface Temperature of Space Plane

Structural materials with properties not found in existing materials—like high specific strength, high specific rigidity, heat resistance, shock resistance, superior heat fatigue properties, and anti-acid corrosiveness under extreme environmental conditions like ultrahigh temperatures—will be necessary and vital for realizing these projects. Of these, the most desirable

development would be a lightweight structural material that can withstand high temperatures of 1,000~2,000°C for use in the space plane body, its engine, gas turbines, and wings, and in the walls of nuclear fusion furnaces (Figure 1).

Work in this area is being actively pursued in America and Europe in view of the great expectations for the realization of the space plane and SST/HST by the beginning of the 21st century, as a means of high-speed transportation. One of the key technologies in this development effort is a heat-resistant structure that can withstand the extremely high temperatures that accompany high speeds. The key to the design of such structures is material technology.

America's NASP, Germany's SANGER, England's HOTOL, and France's HERMES are some of the space plane projects that are going on now. The most important factor in all these projects is the development of advanced lightweight heat-resistant materials like carbon/carbon (C/C) composites, intermetallic compounds, and fiber-reinforced intermetallic compound composite materials. It is impossible for private institutions to undertake to realize this "super environmental-resistant advanced material" since it requires heavy investments and long periods of research. For this reason, the Agency of Industrial Science and Technology in 1989, launched an eight-year project to pursue R&D on super environmental-resistant advanced materials. This marks the first new materials development project as part of an effort to establish a technical R&D foundation for next-generation basic technologies. This article will describe the current status of this project.

It is important that applications of basic research on material design or material assessment be pursued simultaneously with R&D in material production technologies. It is vital, therefore, that close communications be maintained among industry, government, and the academic sector, and that work progress on a cooperative basis.

The situation is exactly the same for the space plane projects under way in various nations, whose purpose is to develop advanced, lightweight, heat-resistant materials. A consortium of the industrial, governmental, and academic sectors can be established as a national development project.[2,3]

2. R&D Target

There are basic technologies for developing super environmental-resistant advanced materials, like intermetallic compounds and advanced composite materials with superior isotropic strength, acid resistance, anticorrosive-ness, and ductility at high temperatures. The following targets were established for each type of advanced material to be developed:

(1) Development of Intermetallic Compounds

　　1) Intermetallic compounds with high specific strength

　　　　• Specific strength (strength/specific weight) greater than 100 MPa at 1,100°C.
　　　　• Elongation of more than 3 percent at room temperature.

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2) Intermetallic compounds with high melting point

- Tensile strength of more than 75 MPa at 1,800°C.
- Elongation of more than 3 percent at room temperature.

(2) Development of Advanced Composite Materials

1) Carbon fiber/carbon-based composite materials (two-dimensional fiber structure)

- Possesses following mechanical properties after 20 hours of heating at 2,000°C, 1 atm. pressure
  tensile strength: >700 MPa
  tensile modulus of elasticity: >200 GPa
- Possesses above mechanical properties after 200 hours of heating at 1,800°C, 1 atm. pressure.

2) Fiber-reinforced intermetallic compound composite material (UD fiber structure)

- At 1,100°C, tensile strength: >1,200 MPa
  tensile modulus of elasticity: >180 GPa
- Possesses above mechanical properties after 200 hours of heating at 1,000°C, 1 atm. pressure.

(3) Development of Assessment Technology

It is necessary to develop assessment technologies that can be applied to the development of the materials described above. This is subject to the R&D results obtained by the end of the first phase (1989-1992) at which time the targets may be reconsidered and altered.

3. R&D System

The R&D results obtained up to 1990 are shown in Figure 2. Research projects were commissioned out to nine private companies affiliated with the Jisedai Kinzoku/Fukugou Zairyo Kenkyu Kaihatsu Kyoukai (Association for R&D on Next-Generation Metals and Composite Materials) and to eight research centers affiliated with the PEC (Sekiyu Sangyo Kasseika Senta) from six national research laboratories attached to the Agency of Industrial Science and Technology, the Science and Technology Agency, and the New Energy Development Organization (NEDO). The development of common basic technologies were conducted jointly with four national universities.

4. R&D Schedule

This will be an eight-year project. This first phase will be from 1988-1992, while the second phase will be from 1993-1995.

The basics in material design, production process, and techniques will be established during the first phase of intermetallic compound development,
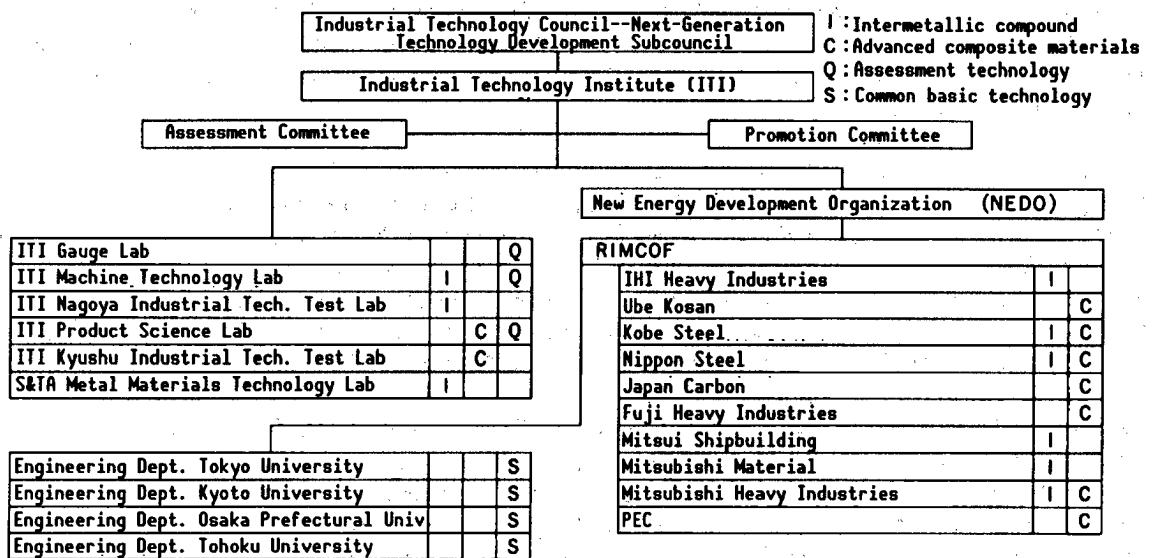
Figure 2. R&D Organization

Industrial Technology Council--Next-Generation Technology Development Subcouncil

Industrial Technology Institute (ITI)

Assessment Committee — Promotion Committee

New Energy Development Organization (NEDO)

I : Intermetallic compound
C : Advanced composite materials
Q : Assessment technology
S : Common basic technology

ITI Gauge Lab			Q
ITI Machine Technology Lab	I		Q
ITI Nagoya Industrial Tech. Test Lab	I		
ITI Product Science Lab		C	Q
ITI Kyushu Industrial Tech. Test Lab		C	
S&TA Metal Materials Technology Lab	I		

RIMCOF		
IHI Heavy Industries	I	
Ube Kosan		C
Kobe Steel	I	C
Nippon Steel	I	C
Japan Carbon		C
Fuji Heavy Industries		C
Mitsui Shipbuilding	I	
Mitsubishi Material	I	
Mitsubishi Heavy Industries	I	C
PEC		C

Engineering Dept. Tokyo University			S
Engineering Dept. Kyoto University			S
Engineering Dept. Osaka Prefectural Univ			S
Engineering Dept. Tohoku University			S

while its design will be upgraded and the production process established during the second phase.

In the case of advanced composite materials, the development of a heat-resistant reinforced fiber, together with basic composition and molding techniques, will be pursued during the first phase. In the second phase, based on the results of the previous stage, the heat-resistant reinforced fiber will be upgraded, and production processes will be established.

During the first phase, techniques to assess the thermal, mechanical, and chemical properties (at high temperatures) of the materials developed will be investigated, while in the second phase, based on the results of the previous phase, actual techniques will be established.

5. Results of R&D to Date

Here we present the results up through 1990. The project began with applications from the private sector during FY89. Consequently, actual research began only at the end of 1989, and lasted for a mere one year and three months.

5.1 Development of Intermetallic Compounds

(1) High Specific Strength of Intermetallic Compounds

The material to be developed is a TiAl-based intermetallic compound. This compound was selected because it is lightweight and features superior acid resistivity and anticorrosiveness. It also is viewed as a promising material for structures in space plane or HST bodies because it maintains its properties even at temperatures as high as 1,100°C. The disadvantage, however, is its poor ductility and workability at normal temperatures. The main target in this project, then, is to improve these shortcomings and to increase its

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thermal and acid resistance at high temperatures. For this, an accurate equilibrium diagram first must be constructed in order to understand the composition, crystal structure, modifications, and the extent to which solid solutions of alien elements can exist.

To improve its ductility at room temperature and its high temperature strength, the effects of a third element on the transformed structure, strain, fracture system, and tempering must be considered on a system basis. At the same time, configuration control and the fineness of the crystal grain must also be considered. Production of intermetallic compounds can be roughly divided into two types: dissolution techniques and hot melted solutions, or powder processing techniques and powder molding techniques.

Analysis of the structure of an active TiAl intermetallic compound at high temperature with the help of a high temperature X-ray analytical device attached to a device for controlling the environment proved (in latest phase diagrams) that an α phase exists at high temperatures. This method was also employed for creating high temperature phase diagrams for TiAl intermetallic compounds. In the future, various basic data will be gathered for the creation of phase diagrams by making similar measurements on materials with various composition at different temperatures. The effects of stoichiometric configuration on the crystal structure and on its mechanical properties will be investigated. At the same time, the effects of a third additive element like V, Cr, Mn, Nb, Mo, or Ta also will be checked.

The TiAl thin sheet production process is one of the techniques that currently is drawing a lot of attention. An outline of the process flow is depicted in Figure 3. The thin sheet production stage consists of (a) the production of a rolled material from a sheet caster in an inert environment, and (b) the production of a thermally rolled material by a constant


Figure 3. General Outline of Process To Make Thin Sheets Directly From Melt

temperature roller. The second molding stage for the thin TiAl sheet is scheduled to be performed in an inert environment that takes advantage of the super plasticity of the material. The success of this process will depend on configuration control T, including the solidification and heating techniques. These techniques will determine the plastic molding capability of thin sheets of TiAl.

The solution and rolling of TiAl is determined on the basis of our understanding of the changes in its behavior when its constituents are changed, the effects of cooling speed on the coagulated composition, as well as from an

analysis of the coagulated configuration. Basic research vital to configuration control, such as configuration change through heat treatment of casted metals or the transformations encountered under high temperatures, also will be pursued. It has been proven that in relation to secondary production, basic work for understanding the effects of composition, configuration, and processing conditions on the plastic transformation of this material is very important. Configuration control (isometric grain refinement) will be vital to improving its workability in the plastic phase. A powder ejection molding method, called the near-net shape method, has been proposed, and thus bonding and cleaning agents are being investigated for use as starting materials.

(2) Intermetallic Compounds With High Melting Points

Aluminide or silicide (Nb or Mo intermetallic compounds with high melting points) are materials that feature superior isotropic strength, acid resistance, anticorrosiveness, and antiabrasiveness at high temperatures. They are attracting a good deal of attention as promising structural materials for movable and stationary engine wings of SSTs or space planes which are subjected to temperatures around 1,800°C. However, research on such intermetallic compounds with high melting points is still in its infancy. At first, potential compounds must be identified. Next, equilibrium diagrams must be created, and the effective configuration be determined. Research must begin only after the crystal structure, physical, chemical, and mechanical characteristics are fully understood. Since intermetallic compounds with high melting points are more brittle than TiAl-based advanced materials, tests to improve their ductility through a search for additive elements that will activate the transformation mode or to understand the crystal structure change most effective for transformation are important.

Let us focus on an Nb-Al-based intermetallic compound, and create a phase diagram for it. Very little research has focused on this, because accurate experiments are difficult to perform because of its extremely high melting point and its extreme instability at high temperatures.

An analytical X-ray device for creating phase diagrams of the Nb-Al-based material placed in a controlled environment whose maximum temperature can reach 2,000°C has been devised. The basic structure of this device is shown in Figure 4.


Figure 4. Basic Structure of Super-high Temperature Phase Diagram Creation Device

Accurate tempering and powdered alloy molding techniques have been developed specifically for this intermetallic compound. A high-temperature dissolution and tempering device will be developed, and a prototype tempering mold has been fabricated. Basic experiments on purification and configuration control through dissolution are being performed. At the same time, a compact plasma

Figure 5. Schematic of Compact Plasma
Dissolution Apparatus
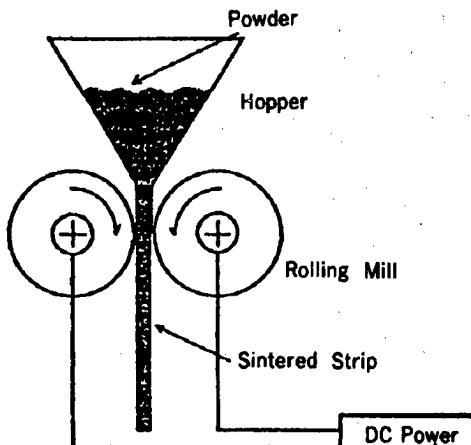
Figure 6. Conceptual Design of
Constant—Temperature Powder
Rolling Device

dissolution gas atomizer device is designed and fabricated. Basic experiments on powder processing were conducted. This atomizer device is shown in Figure 5. Basic research on sintering properties and powder rolling are also performed (Figure 6).

5.2 Development of Advanced Composite Materials

### (1) Carbon Fiber/Carbon-Based Composite Material

C/C composite materials or a carbon—based matrix reinforced by carbon fiber, are capable of resisting temperatures greater than 2,000°C when placed in a nonacidic environment. Such materials are viewed as promising lightweight superheat—resistant materials with high specific strengths at high temperatures and that have high defect and impact tolerances. For example, applications in areas exposed to high temperatures of up to 2,000°C, like in the nose cone of the space plane, the front edges of the wings, and the engine inlet parts, are considered promising. The main disadvantage of this material is the high acid abrasion characteristics of carbon fibers, which makes it necessary to cover the material with an acid—resistant coating.

A complete range of technologies from upgrading carbon fiber performance to covering a C/C composite material with an acid—resistant material must be developed before the targeted properties can be achieved. A total of five types of carbon fibers are used. Three are petroleum pitch—based carbon fibers, while the fourth is coal—based and the last is PAN—based. Eight PEC laboratories (three groups) and three private corporations will execute four categories of research. National research centers will work on the basic processes necessary for improving the performance of C/C composite materials. This includes an understanding of the production conditions for C/C composite material with mesophase as the matrix, clarification of the oxidation process of carbon fibers and C/C composite material and the determination of oxidation inhibitor for the matrix.

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1) Performance upgrade for carbon fibers (petroleum pitch-based)
2) Alteration of matrix properties (oxidation inhibitor and improved carbonification)
3) New molding methods for composite materials, such as the compressed Rejincher method, chemical gas infiltration method, high pressure infiltration and carbonification method, and composite rod molding method
4) Acid-resistant covering technology
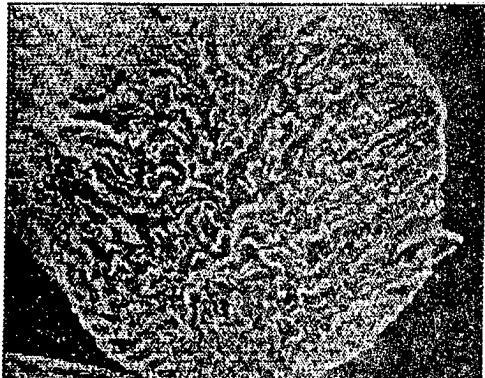
(a) Random structure
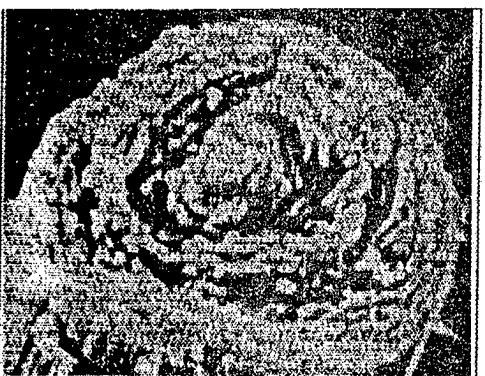
(b) Onion ring structure
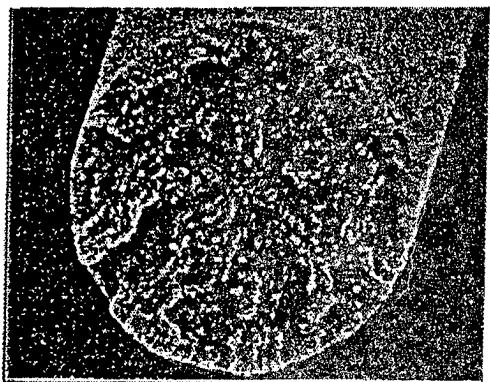
(c) Double layer structure

Figure 7. Structure of Petroleum Pitch-Based Carbon Fiber

Various fiber cross sections, like the random structure, onion ring, or double layer structures, have been proposed by the three PEC laboratories for improving the tensile and compressive strengths of the fiber. Spinning conditions were determined by the laboratories for each type of anticipated cross section (Figure 7). Future work will be on the structure of the cross section to be anticipated for porous fibers. Techniques to cover the fiber surface with a thin ceramic film are being considered as measures to improve the acid resistivity of the carbon fiber itself. SiC covering by the chemical vapor deposition (CVD) method is now an established technique.

In item 2), the basic investigations on improving the carbonization yield by mixing pitch with phenol resin, a matrix forerunner, to improve the compatibility between the fiber and the matrix, as well as to improve the acid resistivity of the fiber through additives like borides, silicides, or preceramic polymers, have been performed.

In item 3), carbonization yield increment (Figure 8) through the pressurized Rejincher method has been confirmed. At the same time, it was observed that the size and shape of residual pores in the porous fiber are influenced by the pressure, Residual pores cannot be avoided in the matrix of a C/C composite material. It is believed that fracturing is closely related to the size and shape of the pores. The adhesiveness between preform and deposited phase during chemical vapor infiltration (CVI) is good, and thus dimensions are not

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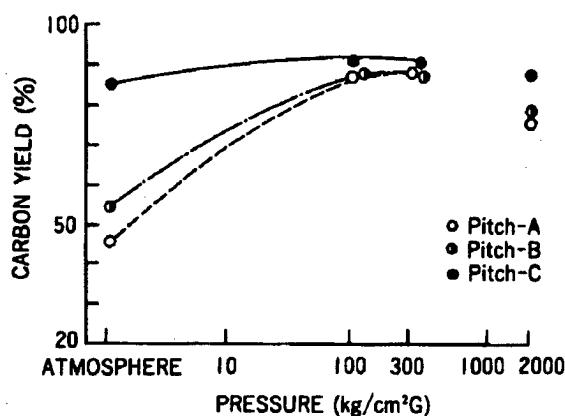
Figure 8. Relationship Between Carbon
Yield and Pressure

Figure 9. SiC Infiltration in
Graphite Sheets by Pressurized
Pulse CVI Method
(SEM cross section)

altered during shaping. Since near-net shaping is also possible, CVI is believed to be a promising method for shaping matrix-packed C/C composite materials. This project aims to increase the deposition speed and to pack more deeply. The two methods of pressurized pulse CVI and temperature gradient CVI are potentially good.

A porous C/C composite material is employed as the preform in the pressurized pulse CVI method, which is believed to improve strength and acid resistivity through SiC packing. Basic packing experiments on graphite sheets or porous C/C materials in a small pulse CVI device have proved that SiC deposition and packing inside the preform is possible (Figure 9).

Infiltration conditions for matrix C into the carbon fiber structure with the help of a filament wind using the temperature gradient CVI method has been determined (Figure 10).

In item 4), the covering techniques for SiC-based materials are established. Preliminary investigations on new acid-resistant materials that remain effective at 2,000°C and coating systems are already under way.


Figure 10. Block Diagram of
Temperature Gradient CVI Device

(2) Fiber Composite Material Reinforced by Intermetallic Compounds

Parallel to the development of a high specific strength intermetallic TiAl compound, work also was under way to develop a SiC Fiber/TiAl-based intermetallic compound composite material using the TiAl compound as the matrix.

The temperature that this material can handle will be that of the intermetallic compound matrix, and it is hoped that its specific strength and rigidity can be significantly improved through fiber reinforcement. Research in this area can be categorized into three interrelated groups. Results of work on high specific strength intermetallic compounds will be implemented in the primary research sector in the following order:

1) Development of high-performance (high strength and acid resistivity) SiC-based fibers
2) Improvement of fiber-matrix compatibility
3) Development of composition and shaping techniques

In the first category, the oxygen content in both SiC (PC) and SiMC (PC) fibers has been lowered significantly (thus rendering them infusible) by electron beam irradiation, thereby creating a highly heat-resistant SiC-based fiber (Figure 11).

Researchers working in the second category have explored the possibility of using barrier materials to suppress reactions between fibers and the matrix at the boundary, and have narrowed their search to metals with high melting points and a few types of ceramics.

Figure 11. Effects of Oxygen Content in Fiber on Tensile Strength After Being Heated for One Hour at 1,500°C and 1 Atmospheric Pressure

The conclusion reached in item three was that HIP molding of a flame-coated preform is the optimum method for fabricating composite materials. Preform processing conditions for flame coating matrix materials are already being investigated. Further, basic experiments to deposit titanium from the raw material by the vapor phase method have been performed to develop a three-dimensional, heat-resistant fiber cloth and to create compositing techniques suitable for the CVI method.

5.3 Assessment Technology

It is believed that fracturing in materials subjected to extreme environmental conditions like very high temperatures is completely different from when it occurs under normal conditions. The characteristics of these superheat-resistant materials must cover a wide range of temperatures and loading conditions. In other words, assessments have many variable parameters.

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In particular, the development of assessment techniques is most important since such techniques do not exist, and there is almost no data on the behavior of such materials at high temperatures. For this reason, measurement techniques for thermal characteristics of materials at high temperatures are being developed. At the same time, techniques to assess the mechanical characteristics, anticorrosion, and acid resistance of such materials at extremely high temperatures, already are being developed.

Methods to measure such heat characteristics as emissivity, thermal diffusivity, and the coefficient of thermal expansion are being developed now. Emissivity was successfully measured up to temperatures of 1,200°C with the help of a semispherical mirror.

6. Conclusion

In general, the development of new materials will lead to the creation of a new industry. Historically speaking, the development of new materials and their implementation have always taken many years. The development of an "advanced material resistant to extreme environments" as undertaken in this project will not be easy. We are confident that through active research and close communication between the industrial, governmental, and academic sectors, good results can be achieved. The following effects are expected through the establish of basic technologies.

(1) Space and Aeronautical Sector

The space plane will fly at speeds of more than Mach 5, and its body temperature is expected to reach more than 1,800°C when flying through the atmosphere. The nose cone and front edges of the main wings of the SST/HST also will reach extremely high temperatures after long periods of exposure. There also will be a demand to raise the combustion temperature in the engine to increase propulsion.

The extreme environment resistant advanced material can be employed in these parts, thereby leading to the realization of the space plane and the SST/HST.

(2) Energy Sector

The extreme environment advanced material will have sufficient heat and radiation resistance to be employed in coal gasification electric power generators, atomic power furnaces, and nuclear fusion furnaces. This is a promising material for allowing revolutionary designs, improving the reliability of structures, and facilitating automation.

(3) Elementary Structure Production Sector

Superhigh-temperature furnace, melt furnace, hot press, and HIP techniques that employ the above production process require a heat resistance of more than 2,000°C. The development of advanced materials capable of functioning in extreme environments will make it possible to improve this process and to make it more reliable.

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Acknowledgements

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Development, Application of Superconductive Materials

[Article by Kazuo Fueki, Department of Science and Engineering, Tokyo University of Science]

[Text] 1. Introduction

Superconductivity occurs when the electrical resistance of a substance cooked to extremely low temperatures reaches zero. This phenomenon was first discovered in Hg in 1911 by Kamerlingh Onnes. Superconductivity disappears when the conducting substance is heated to a temperature above a critical temperature, Tc. It also disappears in the presence of a magnetic field stronger than a critical value, Hc, or when a current density stronger than a critical current density, Jc, is applied to the substance. Figure 1 shows the relationship between temperature, magnetic field, and current density. It also depicts the boundary between super and normal conductivity (condition when electrical resistance is not 0). Let us call this the T-J-H boundary surface. Superconductivity occurs when all values are inside the surface, and normal conductivity arises when they are outside. The values for Tc, Hc, and Jc are large. Superconductivity is stronger when the space inside the T-H-J surface is large.

Figure 1. Superconducting T-J-H Critical Surface Plane

2. Metal-Based Superconducting Material

The superconducting phenomenon was confirmed in Pb, In, and Sn immediately after it was discovered in Hg. However, the Tc and Hc_2 (upper limit for critical magnetic field) values of these elements were too small to be practical. Superconducting magnets became a reality after the discovery of alloys and intermetallic compounds with Nb or V as the main constituent by Matthias, et al., in the latter half of the 1950s.

Metal-based superconductors can be roughly divided into three types: elements, alloys, and intermetallic compounds. The Tc and Hc$_2$ values for the main types of superconductors are shown in Figure 2. It is clear that Nb-Ti alloy has some superconducting properties, since its Tc is about 10 K and Hc$_2$ (at 4.2 K) is about 11 T. A superconducting material will not be feasible unless it has superior superconducting and workable properties. Nb-Ti alloy was widely used from the beginning as it is a highly workable material, and today it is the main constituent in wires. Nb-Ti alloy can be easily fabricated into very thin, multicore wires, and is not susceptible to distortions. In other words, its shape is stable. The ratio of Nb to Ti in the alloy is 50-70. Its configuration is strongly influenced by its workability and heat treatment, and consequently, appropriate conditions must be selected before a desired configuration can be obtained.

The strongest magnetic field that can be generated by Nb-Ti alloy is 10 T, and this can be further strengthened only through the use of intermetallic compounds. This was the impetus behind the development of V$_3$Sn and V$_3$Ga wires. The surface dispersion method and the composite method have been used to fabricate these intermetallic compounds, as they are brittle. In the surface dispersion method, the V or Nb tape is continuously fused and plated with Sn or Ga. Dispersion occurs after heat-resistant to form a superconducting layer of Nb$_3$Sn or V$_3$Ga on the tape's surface. In the composite method, however, the C-Sn or Cu-Ga alloy is fabricated first, and then Nb or V is added to produce a metal composite material that is made into the final wire. This composite is heat treated such that the Sn or Ga in the Cu alloy reacts with the Nb or V, respectively, to form a layer of Nb$_3$Sn or V$_3$Ga compound.
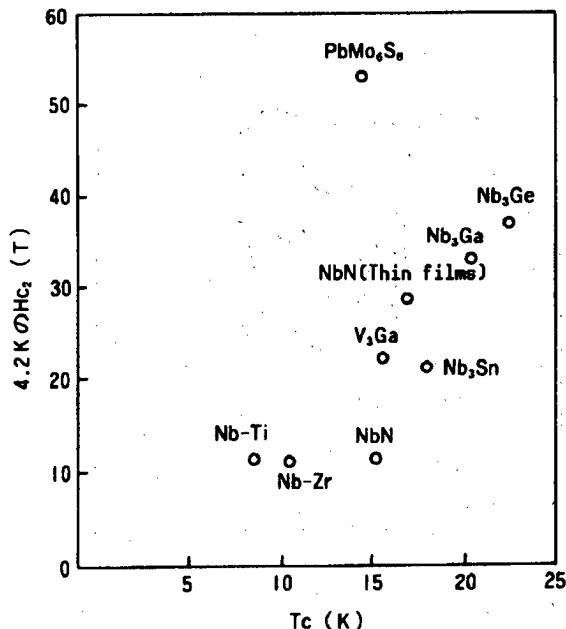

Figure 2. Tc and Hc$_2$ of Metal-Based Superconducting Material at 4.2 K
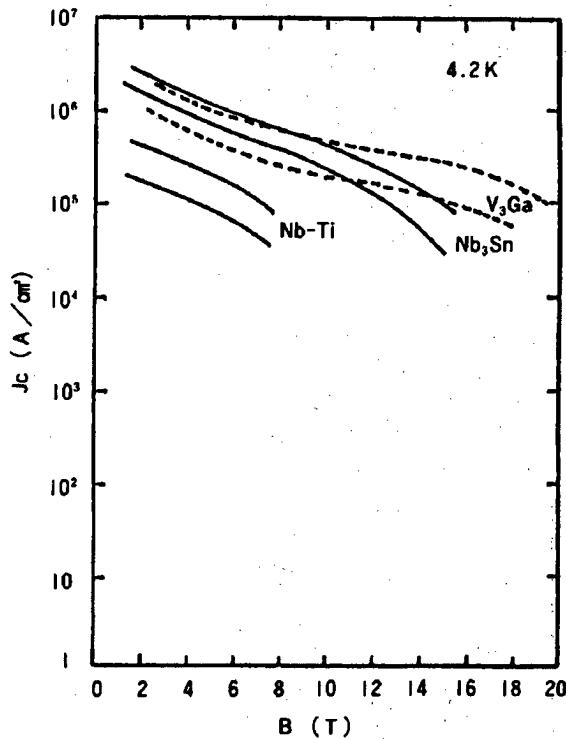

Figure 3. Relationship Between Jc and Magnetic Field for Metal-Based Superconducting Material

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This composite method is suitable for fabricating complex shapes like multicore wires. The Jc of wires made from Cu–Sn and Nb by the composite method decreases when a strong magnetic field is applied. This disadvantage was reduced through the addition of Ti in the Cu–Sn alloy or Nb. Efforts are being made to improve the Jc values of superconductors in the presence of strong magnetic fields. Figure 3 shows the relationship between Jc and the magnetic field of a metal–based superconducting material at 4.2 K.

3. High-Temperature Superconducting Oxides

Bednorz and Mueller's discovery of La–Ba–Cu–O based alloy in 1986 was followed by the discovery of a new copper–based superconductor. Today, there are about 30 types of superconductors, some of which have obtained a maximum Tc of 125 K. This is an amazing feat considering the fact that, until a few years ago, metal–based materials only had a maximum Tc of 23 K. Research and development work on high–temperature superconductors covers a wide range of themes, from fundamentals like the superconductivity mechanism to applications in, for example, wires or electronics. Progress also has been remarkable. At present, however, no practical applications exist.

In the following sections, we will describe the research and development achieved to date.

3.1 Types of High-Temperature Superconducting Oxides

(1) Structure

Table 1. Principal High–Temperature Superconductors

Name	Designation	Chemical formula	Tc	Structure
La-based	214	$(La_{1-x}Srx)_2CuO_4$	40 K	I
	326			
	212	$(La, Sr)_2CaCu_2O_6$	60 K	II
Nd-based	214	$(Nd, Ce)_2CuO_4$	20 K	V
Y-based	123	$YBa_2Cu_3O_7$	94 K	II – c
	247	$Y_2Ba_4Cu_7O_y$	68 K	II –c– II –d
	124			
	248	$Y_2(Ba, Ca)_4Cu_3O_y$	90 K	II – d
Bi-based	2212	$Bi_2Sr_2CaCu_2O_7$	80 K	II – b
	2223	$(Bi, Pb)_2Sr_2Ca_2Cu_3O_y$	110 K	III – b
Tl-based	2212	$Tl_2Ba_2SrCu_2O_y$	105 K	II – b
	2223	$Tl_2Ba_2Sr_2Cu_3O_y$	125 K	III – b
	1212	$TlBa_2SrCu_2O_y$	91 K	II – a
	1223	$TlBa_2Sr_2Cu_3O_y$	122 K	III – a
Pb-based	3212	$Pb_2Sr_2(Y, Ca)Cu_3O_y$	80 K	II – e
	2212	$(Pb, Cu)_2(Sr, Ba)_2(Y, Ca)Cu_2O_7$	32 K	II – f
	1212	$(Pb, Cu)(Sr, Ba)_2(Y, Ca)Cu_2O_7$	20 K	II – a
	1212	$(Pb, Sr)(Sr, Ba)_2(Y, Ca)Cu_2O_7$	53K	II – a
	2222	$Bi_2Sr_2(Ln_{1-x}Ce_x)_2CU_2O_y$	40 K	VI – b

a) Octohedral structure and its connection

BO_2
AO

b) AO and BO_2 lamina

⊕ A   ● B   ○ O
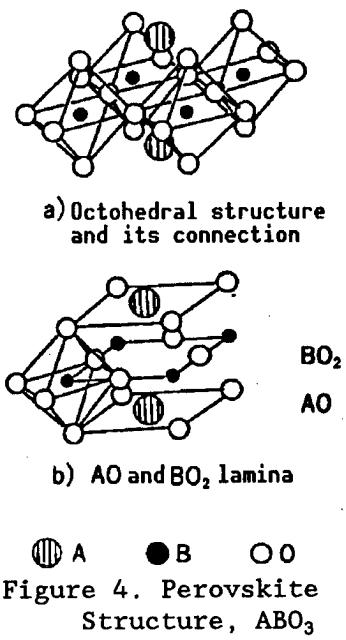
Figure 4. Perovskite Structure, ABO_3

Table 1 lists the principal high–temperature supercon-ductors (discovered to date) and their Tc.

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A high-temperature superconductor has the perovskite (ABO_3) microstructure with Cu in its B site. The perovskite structure is shown in Figure 4(a) where the center of the oxygen ions has a B ion. Each octohedron is connected to six others by a common oxygen ion to become a three-dimensional structure. The crevice created by eight of these octohedrons is filled by A ions. As is shown by the perovskite structure in Figure 4(b), the AO (one A, one O) and BO_2 (one B and two O) atomic planes are arranged alternately. This laminated atomic plane concept is convenient for understanding the structure of high-temperature superconducting oxides, and for this reason, will be employed hereafter.
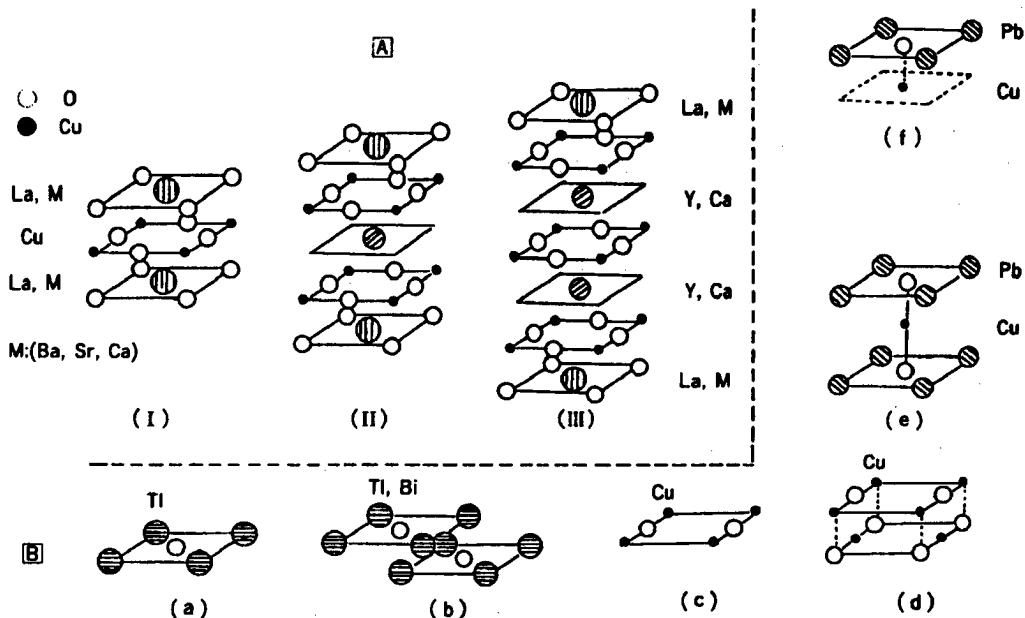
Figure 5. Microstructure of [A] and [B] Units of
High-Temperature Superconductor

The chemical formula for the so-called Y-based 123 is $YBa_2Cu_3O_7$. It has a high Tc of 94 K. The structure of the [A] Group II in Figure 5 is $AO-BO_2-A'-BO_2-AO$. By replacing A with Ba, A' with Y, and B with Cu, the laminated structure of a unit cell becomes $BaO-CuO_2-Y-CuO_2-BaO-CuO$. This is also called $YBa_2Cu_3O_7$, or Y-based 123. The Cu ion of the structure in (c) is directly above the O of the OA plane in (II) when (II) is placed over (c).

The so-called Y-based 248 or 124 oxide has (II) over (d), to become $BaO-CuO_2-Y-CuO_2-BaO-Cu_2O_2$ or $YBa_2Cu_4O_8$. The unit cell is twice this, thereby resulting in a chemical formula like $Y_2Ba_4Cu_8O_{16}$. The Tc for Y-based 124 is 80 K. By replacing Ba with Ca to form $Y_2(Ba,Ca)_4Cu_8O_{16}$, the Tc is raised to 90 K.

Next, let us focus on Bi-based 2212. This oxide is formed by overlapping [A] Group (II) with [B] Group (b) to become $(BiO)_2-SrO-CuO_2-Ca-CuO_2-Ca-Cu_0-SrO$ (Figure 6). The oxygen in the Y plane of $YBa_2Cu_3O_7$, and in the Caplane of the (2212) phase is missing. In general, Y and Ca tend to form "oxygenless" atomic planes, and it becomes $Bi_2Sr_2CaCu_2O_8$, or, in short, Bi-based 2212. Bi-based 2223 phase has a high Tc of 110 K. Its structure is an overlapping of [A] Group (III) and [B] Group (b) to form $(BiO)_2-SrO-CuO_2-Ca-CuO_2-Ca-CuO_2-SrO$, or $Bi_2-Sr_2Ca_2Cu_3Oy$.

Tl-based 2212 phase has a microstructure similar to that of Bi-based 2212 phase where the Bi, Sr, and Ca in the Bi-based material are replaced by Tl, Ba, and Sr, respectively. Similarly, Tl-based 2223 phase has the same microstructure as Bi-based 2223 phase, where the Bi is replaced by Tl, Sr by Ba, and Ca by Sr. Tl-based 1212 has alternate layers of (a) [instead of (b)] and (II), while 1223 phase has (a) and (III).

The planes (I), (II), and (III) of [A] have one, two, and three layers of CuO_2, respectively. Electric charge carriers move within the plane to facilitate conductivity or superconductivity.

(2) Relationship Between Oxygen Content and Tc
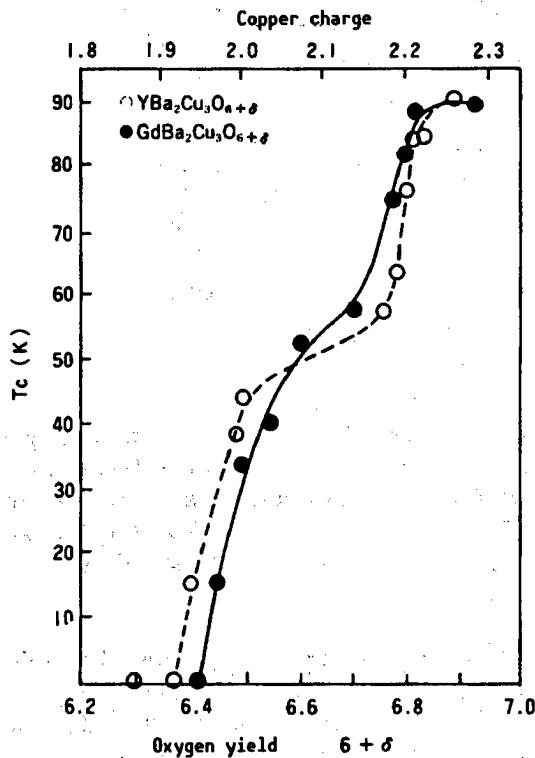
Figure 7. Relationship Between Oxygen Yield and Tc of $YBa_2Cu_3O_{6+\delta}$ and $GdBa_2Cu_3O_{6+\delta}$

Figure 6. Structure of $Bi_2Sr_2CaCu2O_8$

High-temperature superconducting oxides possess non-single-charged ions like Bi, Tl, or Pb in addition to the Cu ion. Cu ions have charges like +1, +2, or +3; Bi has +3 or +5; Tl has +1 or +3; while Pb has +2 or +4. High-temperature superconducting oxides usually have a mixture of differently charged ions with charges higher than two. The average charge has a close relationship with oxygen content. Figure 7 shows the change in the Tc of $YBa_2Cu_3O_{6+\delta}$ and $DyBa_2Cu_3O_{6+\delta}$ at 90 K with variations in the average Cu charge with the oxygen content. Tc rises and then remains constant with a rise in the average charge of Cu. Figures 8 and 9 depict the relationship between the oxygen content and Tc (starting temperature) of Bi-based 2212 phase and 2223 phase, respectively. It is clear from these figures that there is a very close relationship between oxygen content and Tc. From this, we now know that oxygen annealing under appropriate conditions must be performed before a high Tc value can be obtained for high-temperature superconducting oxides.

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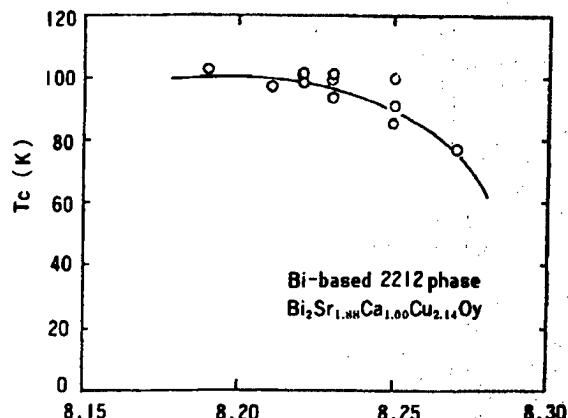
Figure 8. Relationship Between Oxygen
Yield and Tc for Bi–Based
2212 Phase
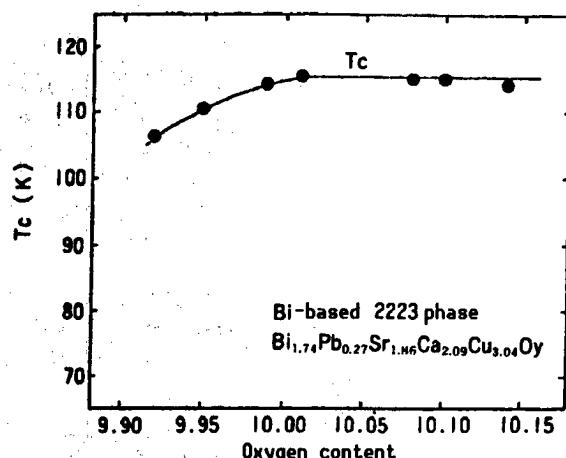
Figure 9. Relationship Between Oxygen
Content and Tc for Bi–Based
2223 Phase

(3) Hc_2

Both Tc and Hc_2 are high for high-temperature superconducting oxides. Table 2 lists the Hc_2 for several such oxides. As is evident from their structures, high-temperature superconducting oxides have laminated structures where the physical characteristics within the ab plane and along the C axis are different. In other words, anisotrophy exists. In the same manner, Hc_2 is also anisotropic. The Hc_2 that results when a magnetic field is applied to the ab plane is usually several hundred T larger when the field is applied along the C axis.

Table 2. Hc_2 of High–Temperature Superconducting Oxides

	Hc_2 (T)
$La_{1-x}Sr_xCuO_{4-\delta}$	‖ C 24 ⊥ C 125
YBa_2Cu_3Oy	‖ C 56 ⊥ C 190
$Bi_2Sr_2CaCu_2O_{8+\delta}$	‖ C 21 ⊥ C 400

(4) Jc

Jc originally was an almost negligible value, but it increased with improvements. Unlike Tc, which has physical characteristics, Jc has material characteristics that are largely influenced by the microstructure of the superconductor. There have been many endeavors to increase Jc values. YBCO-based thin films have been reported to have high Jc values of 8,000,000 A/cm^2 at 77 K. It also performs well in magnetic fields. Values of 1,000,000 A/cm^2

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at 1 T, or 65,000 A/cm^2 at 2 T have been reported. The use of fusion-solidification methods has produced good results. This is the QMG method developed by Nippon Steel Corp. The YBCO fabricated by this method will have Y_2BaCuO_3 phase distributed in the aligned YBCO. The Jc value at 77 K when no magnetic field is applied to 10^{5}Acm^2, while a 1 T magnetic field applied along the C axis causes the Jc to become 10^{4}A/cm^2 (Figure 10).
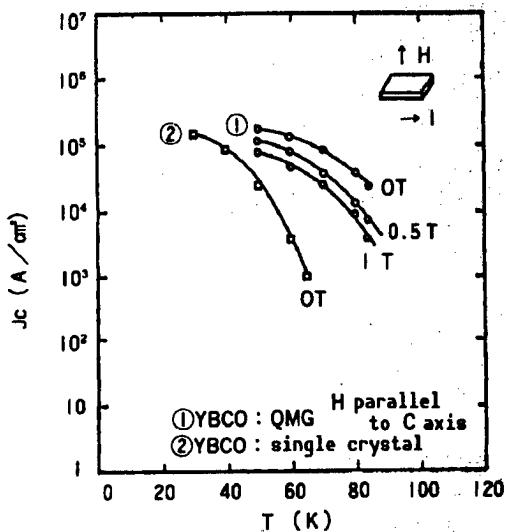
Figure 10. Relationship Between Jc and Temperature of YBCO Fabricated by QMG Method
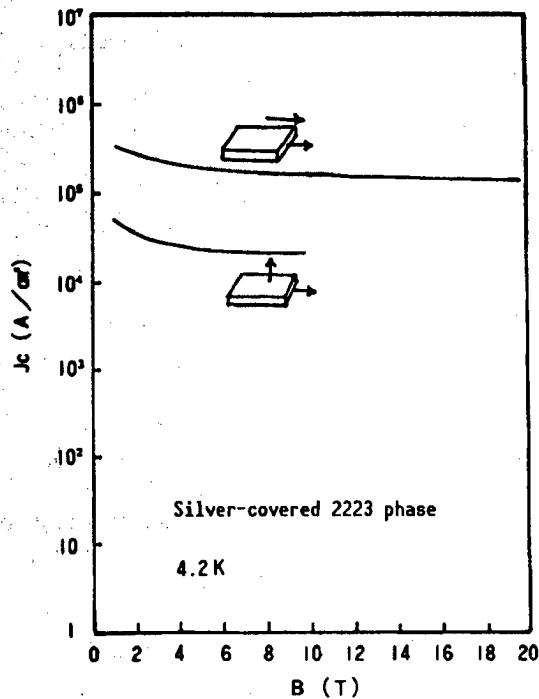
Figure 11. Relationship Between Jc and Strength of Magnetic Field of Bi–Based Silver Covered 2223 Phase
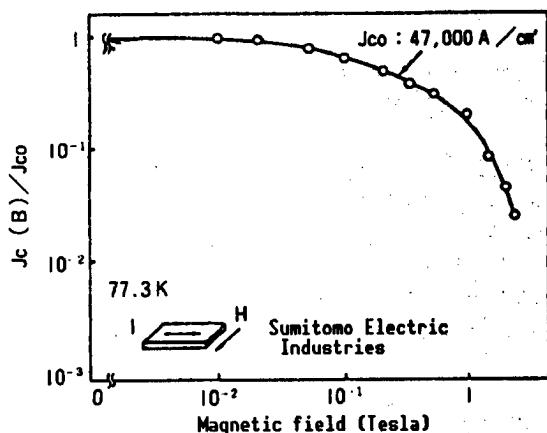
Figure 12. Magnetic Field Characteristics of Critical Electric Current Density

Most Bi–based materials are fabricated by placing the powder in a silver sheath, which is then rolled and partially fused and solidified. The C axis of the oxides in such tapes is usually perpendicular to the silver surface.

As shown in Figure 11, Jc values are high at 4.2 K. For instance, a 20 T magnetic field applied perpendicularly to the C axis results in Jc values of 10^{5}A/cm$_2$. This value exceeds that displayed by metal–based Nb_3Sn superconductors. The anisotropy is large, and when a magnetic field is applied along the C axis, Jc becomes 10^{4}A/cm. However, Jc becomes significantly lower when the temperature rises. This is because the magnetic flux that is restrained by the normal conducting phase is released by the high temperatures. Various restraining mechanisms are being investigated. A good example of the temperature

characteristics is shown in Figure 12. A large Jc value of 47,000 A/cm^2 at 77 K is shown in the figure. When a magnetic field of about 1 T is applied along the sheath direction at the same temperature, Jc drops to about one-tenth the aforementioned value.

A material is usually required to have a range of characteristics. Superconductors are required to display superior workability, mechanical strength, and durability, in addition to its conductivity. Future technical developments in all these areas should be closely followed.

4. Superconductor Application

The relationship between superconductivity and its applications is shown in Figure 13. The Jc value required in the electronics sector is high, 10^{6}A/cm^2, although its magnetic field is small. In the case of strong fields of 10~10^2 T, Jc values of 10^4~10^5 A/cm^2 will be required.

Figure 13. Application in Superconducting Wire Material and Jc-B Range

A determination of the stage of developments attained can be made by comparing, in Figure 13, the superconductivities of metal-based and oxide-based superconductors with the target goals. Significant developments in the characteristics of superconductors should be tracked closely.

Advanced Materials With Space, Aeronautical Applications

[Article by Toshio Nagasawa and Taketami Yamamura, Inorganic Materials Laboratory, R&D Center, Ube Kosan Co., Ltd.]

[Text] 1. **Introduction**

New structural and functional materials for use in aeronautical and space vehicles, instruments, and space structures must be resistant to extremely high and low temperatures and have specific strengths and specific rigidity. These materials also must be dimensionally and chemically stable; resistant to sudden drastic changes in the environment; consistent in their quality; very workable, especially when fabricating large structures; and low in cost.

In an effort to meet these requirements, developments have been made in metallic or metal matrix composites (MMC). These include Al-Li alloy, Ti alloy, intermetallic compound (IMC), superheat-resistant crystal compounds, and heat-resistant eutectic alloys, functionally gradient material (FGM), polymer matrix composites (PMC) like carbon fiber-reinforced polyimide (CFRP), ceramics and ceramics matrix composite materials (CMC), and carbon fiber /carbon fiber matrix composite materials (C/C). Demand for these materials is sure to increase. This article explores the characteristics of these materials, their commercialization, development status, and future potential.

2. **PMC**

(1) **Epoxy Resinal Composite Materials**

The most popularly employed material in the space and aeronautical sector is, as shown in Figures 1, 2, 3, 4, and 5,[1] the carbon fiber reinforced composite material called CFRP, whose matrix consists of epoxy resin. This composite material can be used as a primary structural material in airplanes only if the fracture strain perpendicular to the fiber axis or its interlaminar cohesion strength is improved. The relationship between CFRP elongation along the 90° direction and matrix resin elongation is already known, but elongation along the 90° direction of commercially marketed products is as yet insufficiently

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Figure 1. AV-8B Harrier

Sine wave girder

CFRP26.2%
Aluminum alloy 47.8%
Other materials 26.0%
Basic structure
weight 2274kg
CFRP weight 596kg

Basic structure (wt%)

CFRP	25
GFRP	4
Al alloy	25
Titanium	19
Steel	9
Others	18
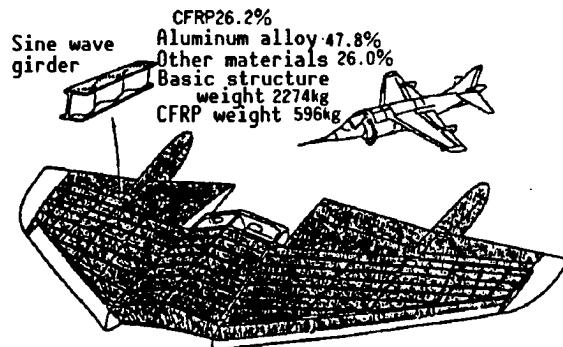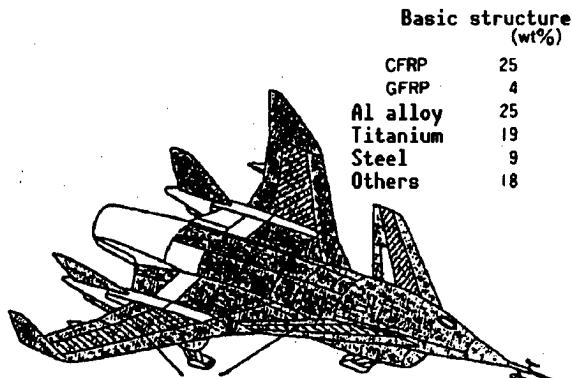
Aerodynamic elastic surface plastics

Figure 2. HiMAT Test Plane

understood. Significant improvements in CFRP interlaminary cohesive strength, meanwhile, has greatly improved its shock/impact resistance. The impact resistance of epoxy resins can be improved through the addition of a rubber component in the resin, but doing so will reduce its modulus of elasticity and also will degrade its thermal resistance and imperviousness to water. As a result, the compressive strength, particularly at high temperatures, of CFRP also will deteriorate. For this reason, research aimed at altering the properties of CFRP and at improving its impact resistance are being conducted by using thermoplastic resin in place of the rubber component.[2] However, thermoplastic resin is incompatible with epoxy resin, and therefore research to alter the properties of the thermoplastic resin must be carried out first.[3]

Outer flap
Outer and inner spoiler
Fixed leading-edge, and trailing panels
Carbon brakes
Pylon fairing
Cowling parts
Nose gear door
Radome
Wing joint fairing

Rudder
Vertical tail
Pivot frame
Horizontal tail
Elevator
Passenger cabin and floor
Flooring material
Main gear door and fairing
Flap fairing
Aileron
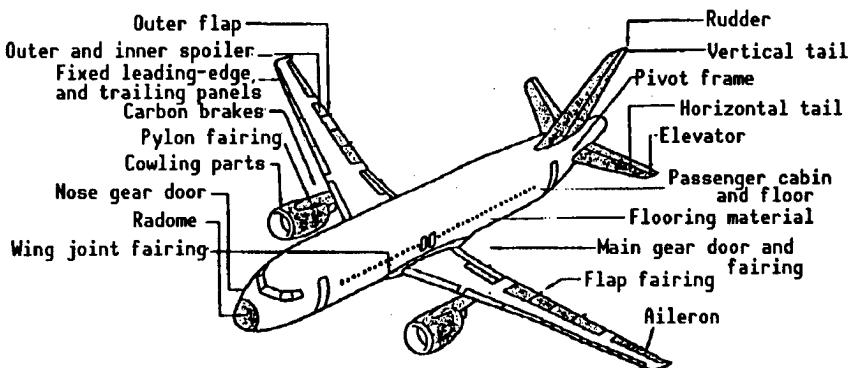
Figure 3. Use of CFRP in A320

Weight reduction accomplished = 1222kg

Outer plate of vertical tail
ΔW=399kg

Elevon
ΔW=483kg

FRCI insulating main flap leading-edge nose cap
ΔW=439kg

Main gear door
ΔW=122kg

STRUCTURE + TPS

Fuselage flap
ΔW=218kg

Weight reduction possible
607kg

Future weight reduction expected = 4849kg

•Main stabilizer wing	1675
•Front fuselage	762
•Central fuselage	1284
•Rear fuselage	1128

Figure 4. Use of CFRP in the Space Shuttle
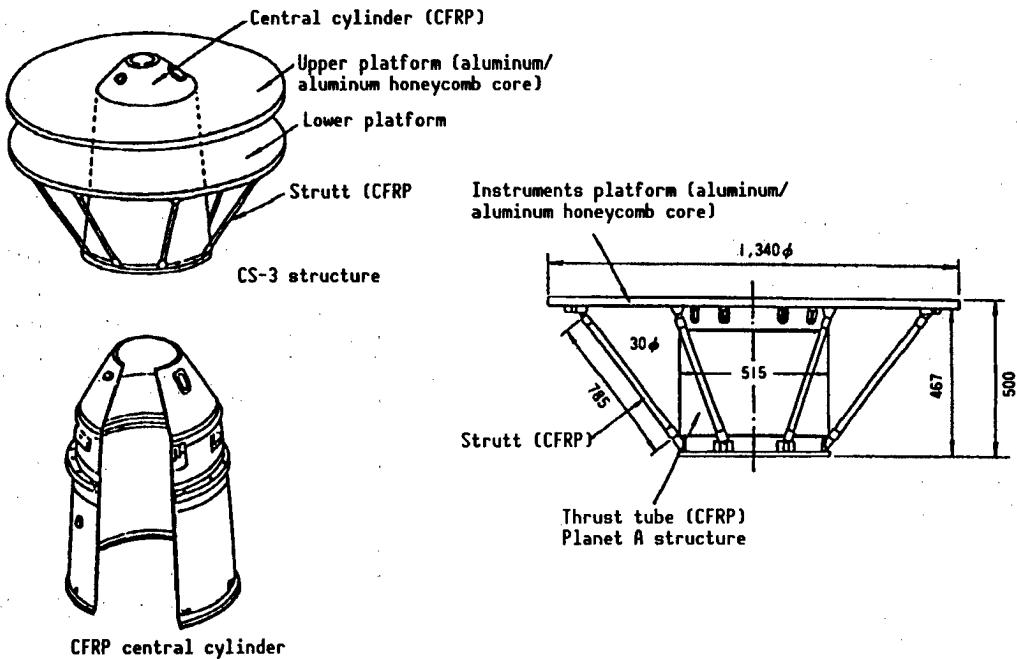
Figure 5. Use of CFRP in Satellite Mainframes

In addition, a method to strengthen the interlaminary cohesive strength of the CFRP prepreg is being performed by introducing a layer of highly workable resin into its lamina. As is evident from Figure 6, this material surpasses the standards required for use as primary structural materials in airplanes.[4]

(2) Heat-Resistant PMC[5]

Bismaleimido resin is as highly workable at 450 K as epoxy resin. It displays a thermal resistance of about 500 K after thermosetting at 503-523 K. Consequently, rapid progress is being made in the development of matrix resins for use in thermal-resistant composite materials.

Figure 6. Shock Resistance of Epoxy Resin

Great advances have been achieved in the development of BMI [4,4-bis(maleimido phenyl) methane] as a CFRP matrix since polyamino bismaleimido resin, a substance with balanced heat resistivity and malleability, was first developed by altering its properties using aromatic diamine. Its commercial marketing was delayed, however, because its malleability did not reach the standards required. Subsequently, a technique, as shown in Figure 7,[5] to metamorphose BMI with a liquid diallyl compound was developed. Based on this, progress was then made toward the fabrication of polymer alloys from bismaleimido resin, thereby improving its malleability.[6] This, in turn, has led to significant achievements in the use of matrix resins in thermal resistant composite materials for use

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Figure 7. Setting Reaction Mechanism for BMI/Diallyl Compounds

Table 1. Characteristics of Highly Ductile BMI Composite Materials

			Hexcel F655/T300	Narmco 5250/IM-7	US Polymeric V 391/IM-7	Ciba-Geigy RX130/IM-8
0°Tensile strength	(MPa)	R T	1722	—	—	—
Bending strength	(MPa)	R T	1976	1545	1544	1790
		177W	1050	718	718	1324
Modulus of elasticity	(GPa)	R T	126	157	158	120
		177W	121	147	148	118
I L S S	(MPa)	R T	139	152	121	123
		177W	56	60	62	68
0°Compressive strength	(MPa)	R T	1633	1724	—	1358
		177W	892	—	—	988
Perforated compressive strength	(MPa)	R T	—	305	434	411
		177W	—	—	359	368
C A I	(MPa)	1000	207	242	—	213
		1500	163	207	233	185

W : Wet

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in spacecraft and aircraft, and in instruments. Table 1[5] summarizes the properties of the latest highly malleable bismaleimido composite material.

The polyimide resin developed in the 1960s is a condensation high polymer resin. However, since the matrix in the composite material was not very workable, addition—hardened polyimide resin P13N was developed6 based on the addition reaction of nadic acid. NASA served as the central coordinating body for this effort. However, difficulties in removing the solvent from the P13N, deterioration of the resin's fluidity during molding, and poor workability of the autoclave have prompted the development of an on—site polymerization—type polyimide resin, PMR—15, from its monomers.[7] The condensate water and alcohol produced during the early condensation stage of PMR—15 have low boiling points since the alcohol solvent also has a low boiling point, the volatile components can be removed easily during molding. Moreover, resin fluidity is much better during molding. PMR—15 is the most popular matrix resin for use in CFRP. NASA has pursued further research on polymer alloys. One of these alloys is LaRC—RP40, a polymer alloy that is about four times[8] as malleable as PMR—15. It is made by adding NR150—B2 polymer to PMR—156. Another polymer alloy that is more than five times as malleable as PMR—15 can be made by adding LaRC—TPI to PMR—15.[9] The physical characteristics of PMR—15 and LaRC—RP40 are summarized in Table 2.

Table 2. Properties of LaRC—RP40 and PMR—15 Composite Materials

	LaRC-RP40	PMR-15
Cure temperature(°C)	316	316
Tg, (°C)		
Dry	369	342
Wet	341	325
Equilibrium moisture absorption (%)	1.0	1.3
Flexural strength, GPA (Ksi)		
room temperature as fabricated	1840(267)	1846(268)
316°C as fabricated	1199(174)	1096(159)
316°C after 1500 thermal cycles	1303(189)	744(108)
Flexural Modulus, MPa (Msi)		
room temperature as fabricated	152.3(22.1)	114.4(16.6)
316°C as fabricated	139.2(20.2)	90.9(13.2)
316°C after 1500 thermal cycles	82.7(12.0)	79.9(11.6)
Interlaminar shear strength, GPa (Ksi)		
room temperature as fabricated	97.8(14.2)	110.3(16.0)
316°C as fabricated	47.5 (6.9)	55.1 (8.0)
Shear modulus (dyne/cm³)		
25°C	8.8E+10	5.4E+10
316°C	5.5E+10	3.4E+10
Wt. loss after 1000 hours at 316°C	6.0	5.0
Microcracks after 1000 thermal cycles	0	58

(3) PMC for Use at Ultralow Temperatures[5]

The main applications of PMC as a material for use at ultralow temperatures include liquefied gas tanks or the insulating material in superconducting coils. Figure 8[5] shows the characteristic of stainless 304, a typical ultralow-temperature material together with the strength versus insulating characteristics (thermal conductivity/strength) of PMC. From this figure, it is evident that PMC is a superior ultralow-temperature material. Figure 9[5] shows the relationship between temperature and thermal conductivity of PMC while Figure 10[5] shows a relationship between thermal conductivity and modulus of elasticity of PMC. These figures clearly show that PMC, GFRP, AFRP, and CFRP (in that order) display superior adiabatic properties in ultralow temperatures.
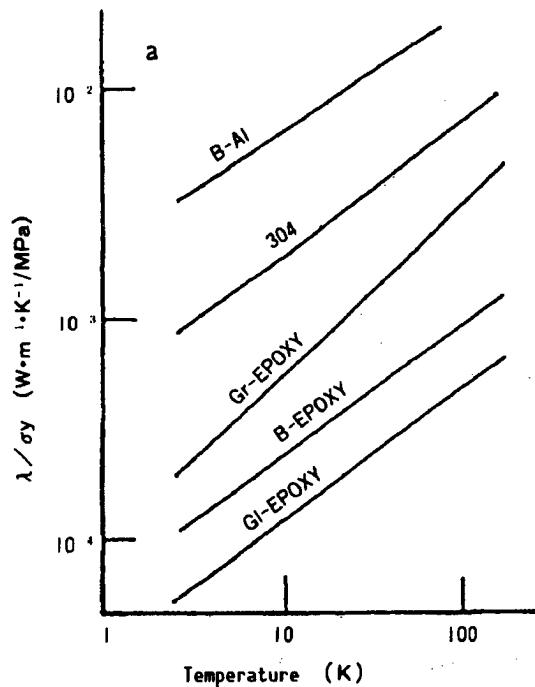
Figure 8. Strength Vs. Heat Insula-
tive Properties of PMC (Thermal
conductivity vs. strength)
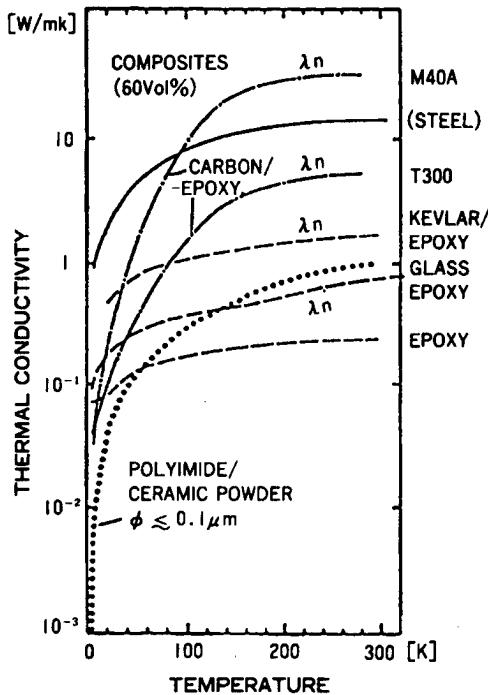
Figure 9. Relationship Between
Temperature and Thermal
Conductivity of PMC

3. Metallic Materials

(1) Aluminum Alloy[10]

Unlike duralumin or super-super duralumin, which becomes heavier when alloyed, Al-Li alloy becomes lighter when alloyed (the weight of an aircraft body decreases by about 10-15 percent when Al alloy is employed) since the density of Li is about 0.5 g/cm^3. In addition, its strength and rigidity also are significantly improved. The Al-Li alloys currently being developed are the three following types:

   1) An alloy that has the strength of duralumin but weighs about 7 percent less;

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25

$\lambda / \sigma_T [\text{m}^2 \text{ SEC}^{-1} \text{ K}^{-1}] \times 10^{-13}$

20

10

5

4.2 K

STEEL

○ Fiberglass/epoxy

△ Carbon fiber/epoxy
(high tensile)

▽ Carbon fiber/epoxy
(high modulus)

□ Kevlar fiber/epoxy

COMPRESSION

Two-dimensional
[quasi-planar . 0°●90°]

TENSION

○ | One-dimensional
| Unidirectional

0   5   10   15

$\lambda / E [\text{m}^2 \text{ SEC}^{-1} \text{K}^{-1}] \times 10^{-11}$ ⟶
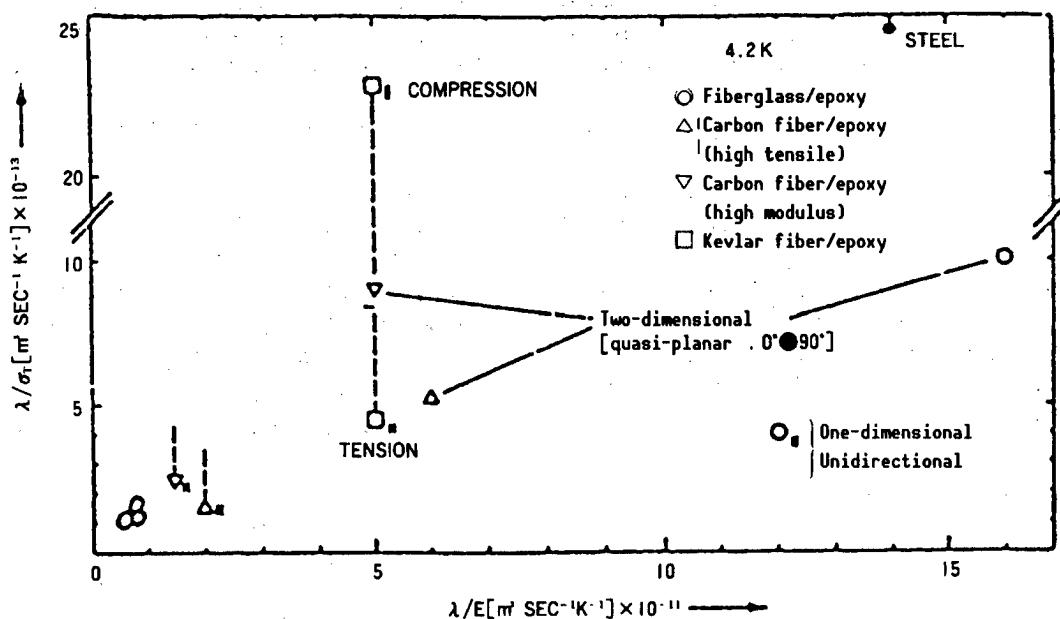
Figure 10. Relationship Between Thermal Conductivity, Strength, and
Modulus of Elasticity

2) An alloy that has the same high tension as super-super duralumin and weighs about 8 percent less; and

3) An alloy that has a specific strength greater than 10 percent, and a specific modulus of elasticity about 20 percent that of conventional strong Al.

For this reason, it is expected that this Al–Li alloy will play a major role as a material for use in aircraft bodies. However, this alloy has a low degree of malleability despite its strength, and this is a major drawback to its practical implementation. These alloys are listed in Table 3.[11]

Alloys that are more malleable than Al–Li alloys are being developed by adding Zr instead of Mn to suppress the coarseness of the crystal grains during recrystallization, and by reducing the Cu content. The mechanical properties of Al alloy are superior at normal temperatures, but they deteriorate significantly once the temperature exceeds 473 K. This deterioration at high temperatures is one of the major problems of Al alloy.

(2) Ti Alloy[5,10,12]

The upper temperature limit where Ti alloy can be used is 723 K. This is very high compared to Al alloy. Its strength is comparable to its high tension network, while its density is 4.5 g/cm³, which is about half that of iron. Consequently, Ti alloy is attracting a lot of attention as a promising material that can withstand extreme conditions, unlike Al alloy. Further, the addition of a few percent of other elements to improve its characteristics will not greatly affect its density, unlike the case of Al alloy.

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Table 3. Characteristics of Typical Al-Li Alloy

Alloy		Composition (wt%)		Structure[1]	Quality	Tensile properties[2]			Toughness Kic kg·mm^{-3/2}	Density ρ g/cm³	Young's modulus E kg/mm²
						σB kg/mm²	$\sigma 0.2$ kg/mm²	δ %			
U.S. Air Force	A	2.3Li,1.4Cu,1.0Mg, 0.2Zr	P/M	E	T 6	50.0	42.0	7.4	—	2.54	—
//	B	1.6Li, 3.0Cu, 0.8Mg, 0.2Zr	P/M	//	T 8	63.5	56.6	10.6	—	2.64	7,850
Alcoa	A	Li, Cu, Mg, Zr	I/M	P	—	45.7 (49.6)	40.1 (38.6)	9 (10)	— (113)	2.55 (2.55)	8,010 (8,150)
//	B	2.2Li, 2.7Cu,0.12Zr	//	//	—	60.5 (56.9)	56.9 (52.0)	9 (9)	106 (89)	2.59 (2.57)	8,010 (7,730)
//	C	Li, Cu,Mg, Zr	//	//	—	45.0 (43.6)	32.1 (30.9)	5 (10)	— (89)	2.52 (2.46)	8,370 (8,150)
//	D	Li, Cu, ZrあるいはLi, Cu, Mg. Zr	//	//	—	53.8 (49.6)	47.8 (42.9)	7 (14)	— (110)	2.55 (2.55)	8,150 (8,150)
Alcan	A	2.5Li, 1.2Cu, 0.7Mg 0.12Zr	//	//	T 8	51.0 (44.9)	42.9 (38.8)	6 (6)	120 (—)	2.53 (—)	8,110 (—)
//	B	2.6Li, 2.0Cu, 0.7Mg, 0.12Zu	//	//	T 8	55.1 (50.0)	49.0 (42.9)	5 (6)	104 (—)	2.55 (—)	8,150 (—)
01420		5.5Mg, 2.1Li, 0.6Mn, 0.18Zr, 0.18Cr	—	—	—	47.6	33.5	9	—	2.47	7,530
2020		4.5Cu,1.2Li, 0.5Mn, 0.2Cd	I/M	—	T 6	59.1	54.2	3	—	2.73	7,880
					TMT	57.1	51.5	13	—	—	—
2014		4.5Cu,0.6Mg,0.9Si, 0.8Mn	//	—	T 651	49.2	42.0	10	81	2.80	7,450
2024		4.4Cu,1.6Mg,0.6Mn.	//	—	T 351	49.5	35.2	18	142	2.77	7,460
					T 851	49.5	45.9	7	78	2.77	7,460
7075		5.6Zn,2.5Mg,1.6Cu, 0.23Cr	//	—	T 6	58.3	51.3	11	89	2.89	7,320
					T 76	54.8	47.8	12	102	2.80	7,320
					T 73	51.3	44.3	13	106	2.80	7,320

(1) Extrusion material：E、Sheet material：P   (2)( )：Value at center of targeted range
( )：Estimated specifications

Ti alloys that are commercially available now can be roughly classified into the three types shown in Table 4.[10] They are α, $\alpha+\beta$, and β types. The α Ti alloy has elements like Al added to its low temperature α phase to improve its stability. It does not display the fragility of other alloys, including during its β phase at high temperatures of about 773 K. The α-Ti alloy also is very easy to weld. Al is mixed near the upper limit of its solid solution (6~8 percent) in order to improve its strength. A sub-α type called super α-Ti alloy also has been developed by adding large amounts of various elements. This material can find application in jet engine parts or large structural elements. Ti-6Al-4V alloy is a typical $\alpha+\beta$ alloy whose metallic microstructure can be significantly adjusted through heat treatment. This alloy is very malleable, easily welded, and highly reliable. Consequently, it is becoming popular as a material for general-purpose aircraft bodies. However, at

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Table 4. Strong Ti Alloy

Type	Alloy composition	Heat treatment	Tensile strength (kgf/mm²)	Notes
	Pure Ti for industrial use	Nonannealed cold processed	25~50	Superior welding property
α phase or sub-α phase	5Al-2.5Sn	Annealing	87	Fair welding property
	8Al-1V-1Mo	//	112	//
	7Al-12Zr	//	116	//
	2.25Al-11Sn-5Zr-0.2Si	//	112	(U.K.)Good high-temperature strength
	6Al-2Sn-4Zr-6Mo	S T A	120	(U.S.)Good quenching property
α+β phase	6Al-4V	Annealing	95	Most widely used
		STA	120	Rollable material, cast material
	4Al-3Mo-1V	S T A	136	Rollable material, welding property deteriorates
	4Al-4Mo-2Sn-0.5Si	STA	125	(U.K.)
	6Al-2Sn-2Zr-2Cr-2Mo-0.25Si	S T A	130	(U.S.)Good quenching property
	5Al-4.5V-2Mo-1Cr-0.6Fe	S T A	185~200	(Russia)Prototype, no toughness
	6Al-6V-2Sn-6Zr-(Cu, Fe)	S T A	133	(France) Prototype
	8Al-4Co	S T A	134	(Japan) Prototype
β phase	13V-11Cr-3Al	S T A	160	(U.S.)
	11Cr-8Mo-3Al	S T A	148	(Russia)
	15Mo-5Zr-3Al	S T A	150	(Japan) Toughness
	11.5Mo-6Zr-4.5Sn	S T A	119	Beta III Very workable (U.S.)
	3Al-8V-6Cr-4Zr-4Mo	S T A	126	Beta C Very questionable (U.S.)

temperatures above 670 K, the strength of this alloy drops drastically. Its workability worsens, and, in some cases, the yield of spare parts production from the cast material to the finished product is less than 10 percent. Cold molding of sheet parts deteriorates, thereby requiring heat molding at temperatures above 1,000 K. Other problems include a high material cost, which is about 10-15 times that of Al alloys. The demand for high-performance materials for use in space and aeronautical equipment has prompted research to focus on very workable Near-β alloy and β alloy. These alloys are more workable than the α alloy. Most of these alloys are strengthened by the time limit deposition method. The β-Ti alloy that has been developed and made commercially available in Japan is Ti-15Mo-5Zr-3Al, while in the United States the corresponding alloy is Ti-15V-3Cr-3Sn-3Al. It is expected that these promising alloys will be adopted for use as structural materials in aircraft bodies in the near future.

A powder metallurgy method that employs rapid cooling and solidification techniques recently has been drawing a lot of attention as a means of significantly improving the performance of Ti alloys. The crystal grains of Ti-6Al-4V are made finer, while its α phase becomes isoaxial when it is rapidly cooled and solidified.[13] A similar phenomenon can be observed in Ti-Mo-Al, which features greatly improved tensile strength.[14] A similar significant increase in strength can be observed in Ti-3Ni-6Al and Ti-15Cr-4Al, or Ti-8V-5Fe-1Al, which are deposited together.[15] A 10 percent increase in strength can be observed in Ti-8V-5Fe-1Al at 1,380 MPa.[16] Ti-25Zr-10Be becomes noncrystalline when rapidly cooled and solidified. In this manner, the anticipated strength at 2,345 MPa can be obtained.[17] Further, noncrystalline Ti-Zr-Ni-Si becomes

crystalline after time limit treat-
ment, thus creating a superfine
microstructure of less than 1 μm.
Results of research on the strengths
of these materials at 2,700 MPa also
are available.[17] As is shown in Fig-
ure 11,[5] the rapid cooling and so-
lidification of Ti-6Al-4V, after
which 1B is added, has resulted in a
highly improved high-temperature
strength[18] through particle distri-
bution caused by the B addition.

(3) Intermetallic Compound (IMC)

Ti-Al intermetallic compounds, espe-
cially Ti$_3$Al or TiAl, which are more
heat-resistant and lighter than Ti
alloy, are now attracting a great
deal of attention. TiAl is more heat
resistant and has higher specific
strengths than Ti$_3$Al. In particular,
it is heat resistant to around 1,270
K. However, this material is not
practical as yet because of its
brittleness at room temperature, and
because of its poor resistance to
acid at high temperatures. In
Japan, these problems have been ad-
dressed in a Jisedai "Super Environ-
mentally-Resistant Advanced Materi-
al" project. The main goal is to
develop a material that possesses
more than 3 percent rollability.[19]

Alloys with relatively high contents
of Nb (Ti 24wt%, Al 11wt%, Nb) have
been developed to overcome the brit-
tleness of Ti$_3$Al at normal tempera-
tures, as shown in Table 5.[5] In the United States, test use of such materials
in prototypes of large aircraft parts already is under way. The present status
of research on the development of Ti$_3$Al and TiAl gas turbine parts in the
United States is shown in Table 6.[5]

Space plane engines require materials that can withstand temperatures of
around 2,270 K. In this regard, intermetallic compounds appear to have high
potential. In particular, Nb$_3$Al, with a high melting temperature of 2,230 K,
and MoSi$_2$, which has an equally high melting point of 2,140 K, are believed to
offer the greatest potential. Nb$_3$Al is an intermetallic compound with an Al5
microstructure. It displays superconductivity, and has a density of 8.0 g/cm^3.
However, Nb$_3$Al itself is brittle, and its acid resistivity is not what one
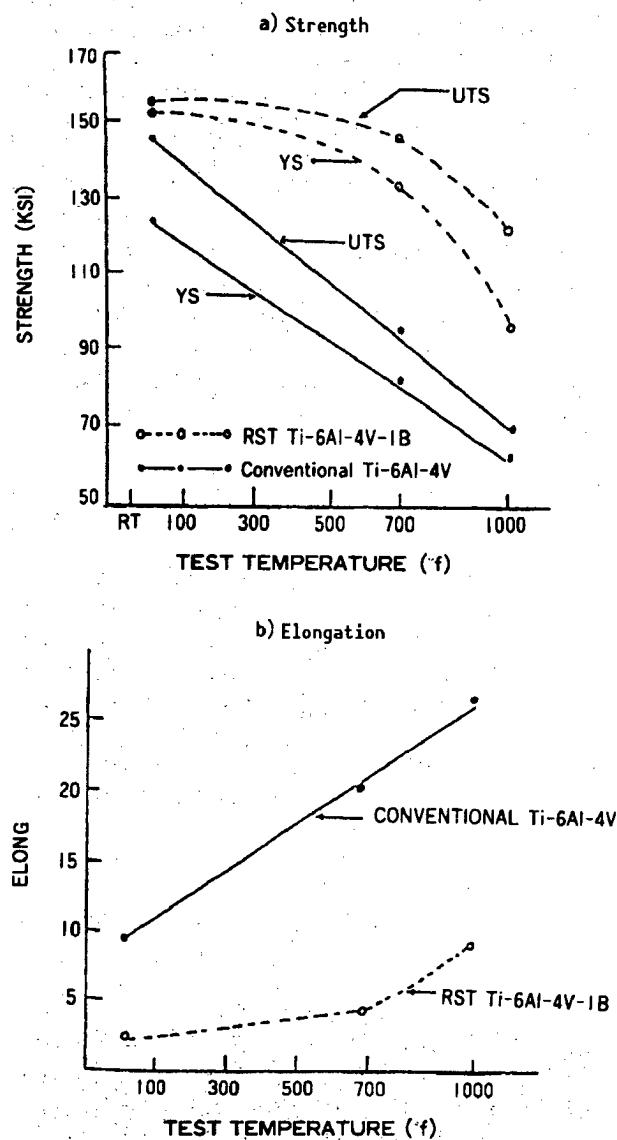

Figure 11. Properties of B-Added
Ti-6Al-4V When Rapidly Cooled

Table 5. Effects of Addition of a Third Element on Properties of TiAl Alloy

Element	Amount (mass%)	Vickers hardness		Deformation ability	Resistance for oxidation
		As cast	Heat treated*		
Nb	30	511	223		
	40	—	242	Brittle	Good
	50	677	—	Very brittle	
	60	—	—		
V	20	511	474	Brittle	Good
Cu	20	446	—	Very brittle	
Fe	30	—	—	Generation	
Ni	30	—	—	of cracks on	
Co	30	—	—	solidifica-tion	
Ag	10	279	171		
	20	285	176	Deformable	
	30	226	129		
	40	209	166		

*Annealed for 604 ks at 1,213 K

would wish for. Further, the difference in the melting points of Nb and Al is large, thus making it difficult to fabricate a homogeneous material. The solution to these problems must be given priority.

(4) Metallic Materials for Use in Engines for Air and Space Planes[10]

The larger the maximum and minimum in temperature and pressure in the internal combustion of a jet engine, the greater its thermal efficiency becomes. The temperature at the mouth of the first turbine was about 1,050 K, but its temperature has increased each year thanks to improvements in material performance. The only metallic materials that can withstand such high temperatures and the burning environment are superheat-resistant alloys with Ni or Co as the base material. The maximum temperature that, for example, state-of-the-art Ni-based superalloy can withstand is about 1,300 K. Figure 12 shows NASA's forecast for progress in heat-resistant turbine blade materials.[20] The alloy currently employed is the superheat-resistant alloy mentioned previously. Future materials will not be completely new, but rather improved versions of existing materials. The leading heat-resistant materials are superheat-resistant alloy with single crystals and heat-resistant eutectic alloys.

The strongest material deposited as a eutectic alloy can be strengthened by the same mechanism as MMC by arranging the deposition to follow a certain

Table 6. Development of Ti₃Al, TiAl Parts for Gas Turbines in the United States

Material	Engine	Part	Fabrication method	Companies in charge of development	Notes
Ti₃Al	F 100	o Afterburner nozzle seal o Compressor casing	o Ultraplastic processing + diffusion welding o Rolling + mechanical processing	Rolling : TIMET Production : Rockwell International Test : P&H	Implement 65hr engine test
"	F 404	Exhaust seal	Ultraplastic processing + diffusion welding		
"	Test engine	o High-pressure turbine stator support ring o Flame container for chamber o Support ring for chamber lining	o Mechanical processing from rolling ring o Precision structure o Rolling	G. E. (Ladish)	Weight reduction by 43% by Rene41 Ti-14Al-21Nb
"	E³ engine	o Sheet metal structural part for mixer and tail cone o External pipe		NASA	Due to insufficient rollability, select parts whose defects are not fatal
"	Small gas turbine	Compressor rotor	Powder metal, HIP (PREP powder, ceramic mold)	Crucible Materials Corp.	Ti-14Al-21Nb
"		"	Powder metal, HIP (powder: PREP)	Nuclear Mctals Inc.	
TiAl	JT9D	Turbine blade	Test production by precision casting		
"	E³ engine	Project to use in low-pressure turbine blade		NASA	Material :MERL10I (TiAl) 900~1100 °F Life > 15.000hr
"			Powder metal, HIP (powder: PREP)	TRW :Nuclear Metals Inc.	Ti-33Al-5Nb-5W

E³ = Energy Efficient Engine
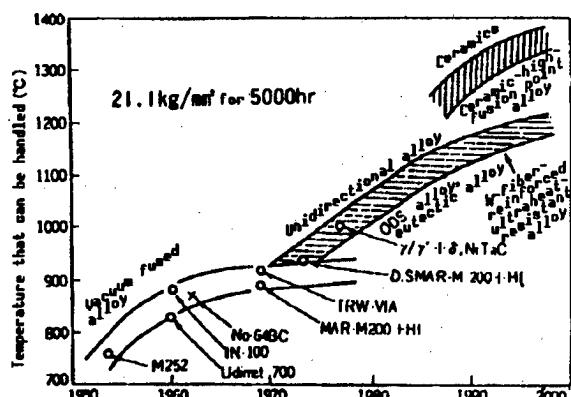


Figure 12. Advancements in Heat–Resistant Materials for Use in Turbine Blades
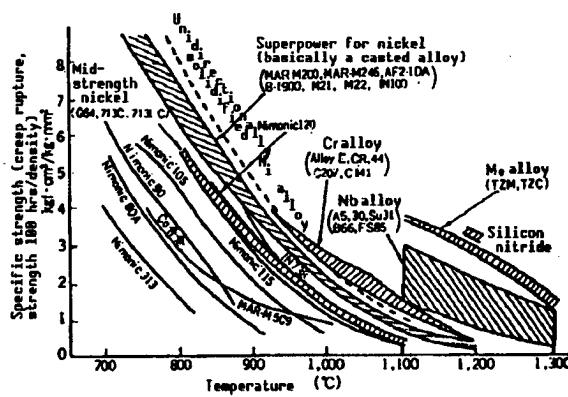
Figure 13. Comparison Between Temperature and Specific Strength of Heat–Resistant Alloy for Use in Movable Blades for Gas Turbines

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direction with the help of a solidification technique. This eutectic alloy is relatively stable at high temperatures, when compared to normal MMC, because of its thermodynamically stable phase. Further, the strengthened phase and matrix bond extremely well. All these alloys are stronger than conventional Ni-based alloys, as illustrated in Figure 13.[21]

In addition to the above, alloys are being strengthened by dispersed particles. These alloys include MA754 alloy with Y_2O_3 distributed in a 20 percent Cr-Ni alloy, MA956 with Y_2O_3 distributed in 20 percent Cr-Fe alloy, and MA6000E with Y_2O_3 distributed in an Ni-based superalloy.

4. Metal Matrix Composites

Polyimide resin is a lightweight, heat-resistant composite resin material for use in space and airplanes at temperatures around 570 K. It has superior specific strengths and rigidity, but when temperatures exceed this point, MMC,
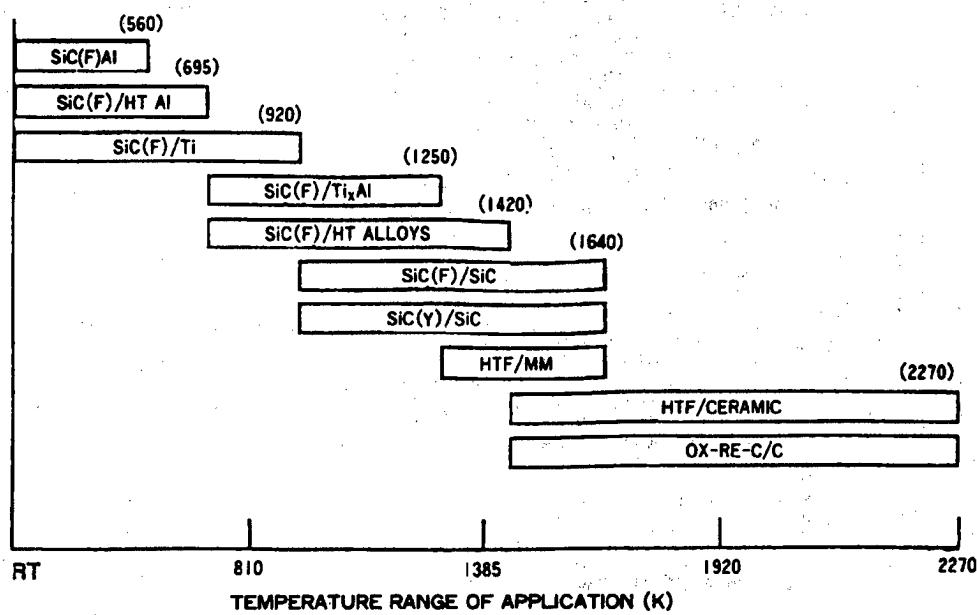
Figure 14. Range of Temperatures That Can Be Handled by MMC and Other Composite Materials

which has a superior heat-resistant matrix, becomes advantageous. As illustrated in Figure 14,[5] low-temperature MMCs include heat-resistant Al-base, Ti-base, Ti-Al intermetallic compound-base, and superalloy-base (including Ni-Al intermetallic compound base). For high temperatures, it shifts to a metal base with a high melting point (including same-based intermetallic compound).

(1) Al-Based MMC[5]

Al-based MMC is the most researched material to date. However, there are very few reports on heat-resistant Al-based composite materials. Figure 15[5] depicts the relationship between the specific strengths and temperature of MMC developed under the Jisedai Project. SiC_{CVD} fiber/heat-resistant Al-based SCS-2/Al-4Ti and SCS-2/Al-8Cr-1Fe displayed the same superior high-temperature strengths as Ti alloy MMC strengthened by SiC fibers (SCS-6) using the same base as the above-mentioned materials. Their specific strengths are aston-ishingly high, showing values of more than 55 km at 700 K.
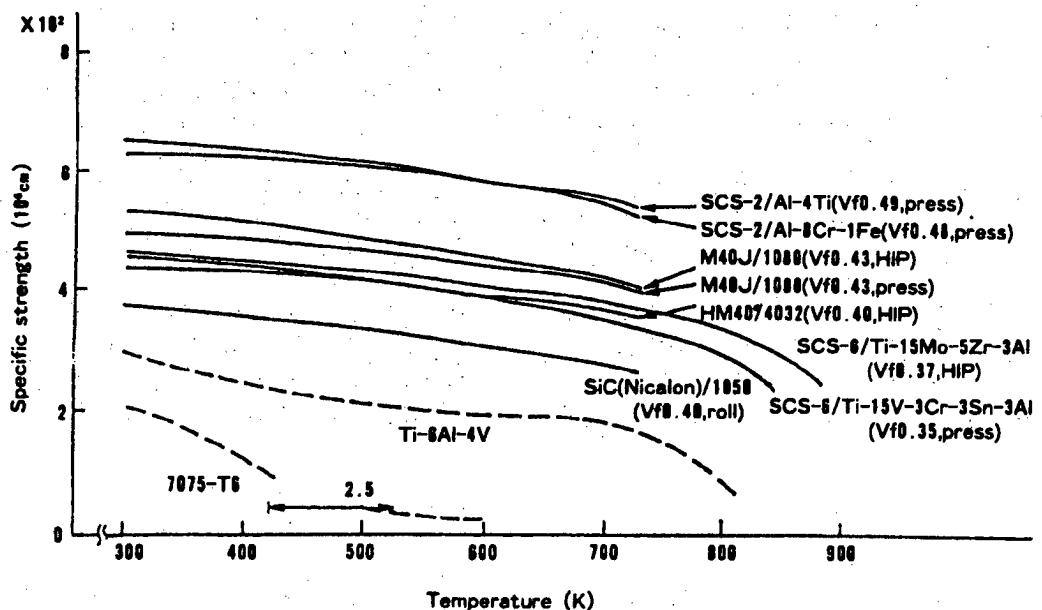
Figure 15. Specific Strength Vs. Temperature of MMC Developed
Under the Jisedai Project

Even heat-resistant Al-based MMC for precursor-type Si-C-O-based fibers
(Nikalon) or Si-Ti-C-O-based fibers (Tyranno fibers) have been developed. Both
have Al-Al$_3$Ni eutectic alloy as the matrix (Nikalon/Al-5.7 Ni,[22] Tyranno/Al-
8Ni[23]). Their strengths are inferior to that of SiC$_{CVD}$-based MMC until about
700 K. They displayed normal temperature strengths, but, on the other hand,
exhibited superior heat resistance. These MMCs are unidirectional (UD)
materials, and their 90° strengths are characteristically higher than other
Al-based MMC.[24]

(2) Ti-Based and Ti-Aluminade-Based MMC[5,25]

Both Ti and Ti-Aluminade are reinforced SiC fibers using the CVD method
(SiC$_{CVD}$). The main type of reinforcement fiber used is the carbon-coated SiCS-
6, as this improves the fiber-matrix compatability. Ti-based MMC is gradually
shifting from Ti-6Al-4V matrix alloy to Ti-15V-3Cr-3Sn-3Al or Ti-10V-2Fe-3Al,
β-alloys. Foil/fiber/foil sandwich hot press, or HIP, is becoming the standard
fabrication method for composite materials. That technology is now almost
complete, and is entering the phase of developing production techniques for
parts used in actual equipment. Boundary reaction advances when SiCS-6/Ti is
heated above 770 K. An increase in the thickness of the reaction layer between
carbides and silicides also was observed. However, the effect on tensile
strength was unexpectedly small. The oxidation of SiCs-6/Ti when heated in the
air has been identified as a major problem. A summary of the characteristics
of SCS-6/Ti-6Al-4V and SCS-6/Ti-15V-3Cr-3Sn-3Al is shown in Table 7.[26]

Research is now under way on Ti$_3$Al(α-2) and TiAl(γ) matrixes in Ti-Aluminade-
based MMC. This MMC is also part of the "Super Environmentally-Resistant
Advanced Material" research under the Jisedai Project sponsored by the
Japanese Ministry of International Trade and Industry. Development work using

Table 7. Characteristics of SCS-6/Ti Alloy
(Sample dimensions: 62 lamina panel)

Mechanical properties of SiC/Ti-6-4 (35v/o)				
	Before heat treatment		After heat treatment (7 hours at 905°C)	
	X	S. D.	X	S. D.
Tensile strength achieved MPa(kgf/mm)	1690 (172)	119.3 (12.1)	1434 (146)	108.9 (11.1)
Modulus of elasticity GPa(tonf/mm)	186.2 (18.9)	7.58 (0.8)	190.3 (19.4)	8.3 (0.9)
Distortion rate	0.96	0.091	0.86	0.087

Mechanical properties of SiC/Ti-15-3-3-3 (38-41v/o)				
	Before heat treatment		After heat treatment (16 hours at 480°C)	
	X	S. D.	X	S. D.
Tensile strength achieved MPa(kgf/mm)	1572 (160)	138 (14)	1951 (198)	96.5 (9.8)
Modulus of elasticity GPa(tonf/mm)	197.9 (20.1)	6.21 (0.7)	213.0 (21.7)	4.83 (0.5)
Distortion rate	—	—	—	—

Nikalon and Tyranno began in 1989. The temperatures that these alloys can handle are 1,090 K and 1,250 K, respectively. Development work involving both MMC and Ti_3Al-based alloy has been undertaken, and Ti-24Al-11Nb, Ti-25Al-13Nb, Ti-25Al-17Nb, and Ti-25Al-10Nb-3V-1Mo have been employed as matrix alloys. The plasma injection method is attracting considerable attention as a preform method for fabricating composite materials, thanks to its ease of fabrication. Despite the amount of research on fiber/matrix boundary reactions in SCS-6/Ti_3Al,[27] there are almost no reports on its mechanical characteristics. A reaction layer results from boundary reaction between carbides and silicides in SCS-6/Ti_3Al. As a result, a β dehydrated area is formed in the neighboring matrix. This area becomes hard, thereby reducing the ductility and strength of the composite material.

(3) Superalloy and Ni-Aluminade MMC[5]

Research on tungsten fiber-reinforced TFRS was initiated in the United States with the goal of using this material in the turbine blades of jet engines. To date, the tungsten fibers have been improved, matrix alloy compatibility research has been performed, techniques for the fabrication of composite materials have been developed, and creep characteristics have been determined. However, such superalloys still are not commonly available, as it has not been possible to raise their maximum temperature by more than 50 K.

Research already has begun on SCS-6, Sigma, and B_4C/B fibers in Ni-Aluminade MMC. Boundary reactions were prominent in all cases, thereby necessitating some sort of barrier coating.[28] For this reason, research is still at the stage of preliminary investigations of the compatibility between the reinforcing fiber and the matrix.

5. Ceramics and Ceramic Matrix Composite (CMC) Material[29]

(1) Unit Ceramics

Of the many unit ceramics that have been developed, oxide ceramics are the most heat and oxidation resistant, and their strength and rigidity at normal temperatures also are high. As shown in Figure 16,[30] their strength drops with temperature. Their specific strength also drops as their density is high, a disadvantageous factor in the airplane industry, which places a premium on lightness. SiC and Si_3N_4 ceramics display superior high resistance compared to oxide ceramics. Therefore, they can be employed at high temperatures. As is clear from Figure 17,[30] Si_3N_4 displays a high level of strength of up to 1,370 K, but above this point SiC is the strongest. One of the factors in the drop in the strength of Si_3N_4 at temperatures above 1,470 K is that the oxide sintering promoter softens at high temperatures. There is a great demand for the development of a new promoter system that can withstand high temperatures.
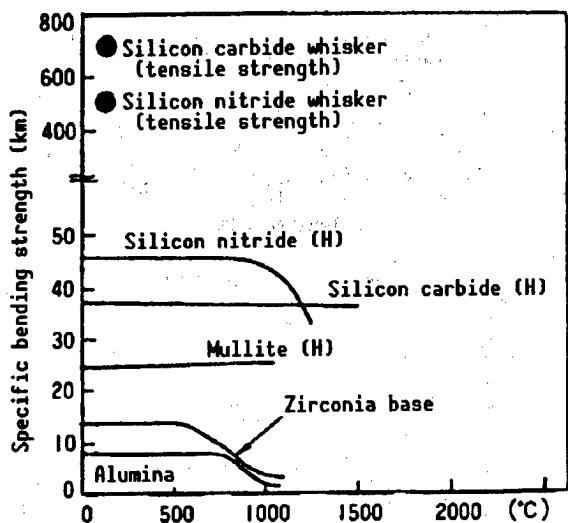
Figure 16. Ceramic Sintered Body and Whisker Strength
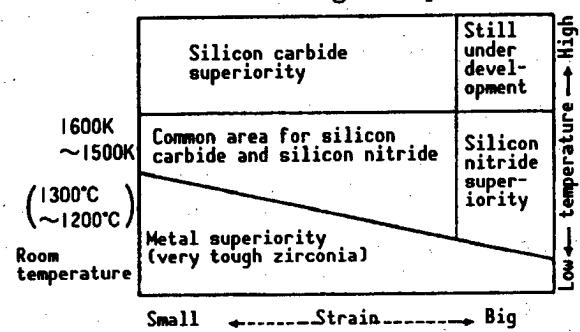
Figure 17. Application Limit for Engineering Ceramics

The toughness, K_{IC}, of Si_3N_4 ceramics is currently 6~8 MPa·m$^{1/2}$. For SiC, this figure is 3~5 MPa·m$^{1/2}$. The former is slightly better. Research is currently being conducted on ways to improve the malleability of Si_3N_4 by distributing nanometer-sized particles in it.[31] The strength and malleability of Si_3N_4 can be improved by distributing SiC particles in it by CVD hot pressing Si-C-N composite powder and a Y_2O_3-Al_2O_3 promoter. Table 8[5] shows the particle content, strength, toughness, and thermal expansion coefficient of Si_3N_4.

Table 8. Mechanical Properties of Si_3N_4 With SiC Particles Distributed in It

Composite	Toughness (MPam$^{1/2}$)	Strength (MPa)	Thermal expansion coefficient($^{\circ}C^{-1}$)	Young's modulus* E(GPa)	ΔTc^{+} ($^{\circ}C$)	ΔTc ($^{\circ}C$)
Si_3N_4	5.5	1100	3.4×10^{-6}	305	1050	1050
Si_3N_4/10vol% SiC	5.7	1130	3.7×10^{-6}	315	857	920
Si_3N_4/25vol% SiC	6.5	1550	4.1×10^{-6}	330	759	800
Si_3N_4/32vol% SiC	6.1	1260	4.2×10^{-6}	340	486	530

*Calculated using a linear relation between E=305 GPa for Si_3N_4 and E=440 GPa for SiC.
+Calculated from strength, thermal conductivity (see Fig. 1), Young's modulus and thermal expansion coefficient. Poisson's ratio was assumed to be 0.25 for all the composites.

The most significant characteristic of unit ceramics is their superior mechanical properties at high temperatures. Others include its oxidation resistance and its dimensional stability (dimensional precision) due to its low thermal expansion. Despite the disadvantages mentioned earlier, ceramics are expected to play a major role as materials in future space planes or supersonic jets that are used under severe conditions. Ceramics are thought to be particularly promising for use as materials in thermal combustion engines or as structural materials in parts of aircraft bodies subjected to high temperature and oxidation. As such, overcoming the biggest disadvantage of ceramics, their brittleness, has become the most immediate problem that must be tackled.

(2) CMC Reinforced by Long Fibers

SiC fiber (Nikalon)/glass CMC developed by United Technologies of America uses borosilicate, high silica gel, or lithium aluminosilicate (LAS) as the matrix. This material is marketed under the name of Compglass. As shown in Figure 18,[32] Compglass displays high values for both its bending strength and K_{IC} when compared to unit LAS matrix. Also, when the newer matrix LAS-III is used, the material becomes one that can withstand oxidation at 1,570 K, as is evident from Figure 19.[33]
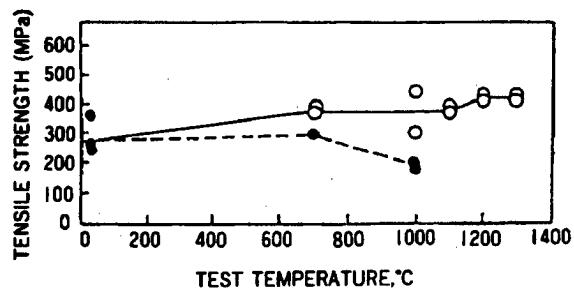
Figure 19. Tensile Strength of SiC Fiber/LAS III Composite Material
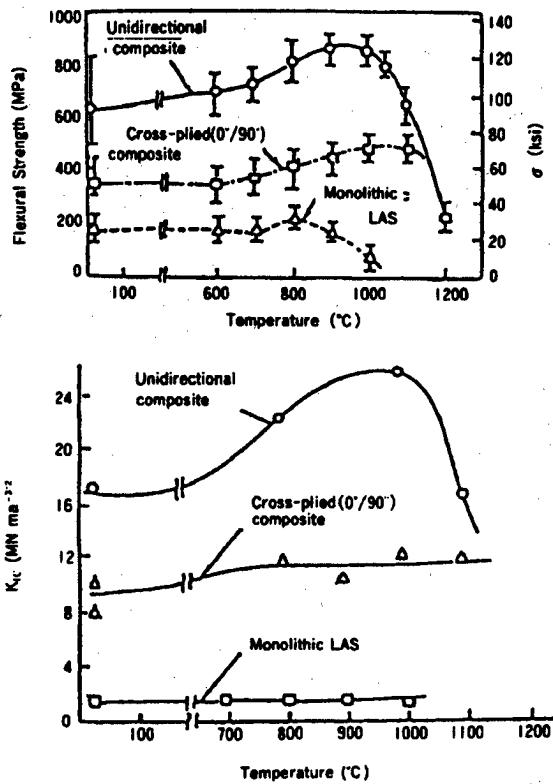
Figure 18. Characteristics of Nikalon-Reinforced Lithium Silicate Glass

The development of SiC fiber/calcium oxide-aluminosilicate (CAS) CMC, which possesses almost the same characteristics as the above-mentioned SiC/LAS CMC, is being pursued in America by Corning Glass.[34] The SiC fiber (Nikalon)/SiC CMC fabricated by the CVI method, which was first developed by the French company SEP and later by Aerospatiale, the United States' Dupont, and Japan's Mitsui Shipbuilding Co., is expected to find applications in the apozimotor nozzle, gas turbine blade, and external tiles of space shuttles, etc., because of its high malleability and the high temperature (1,520 K) it can withstand, as shown in Figure 20.[35]

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Both SEP and Dupont are developing carbon fibers (CF)/SiC CMC using the CVI method. The characteristics of the CMC developed by SEP are illustrated in Figure 21.[36] This CMC is less resistant to oxidation than the above-mentioned Nikalon/SiC CMC, because its reinforcing fiber is carbon. When this material is employed even for a short period in an oxidizing environment, it is stronger with a higher coefficient of elasticity than Nikalon/SiC CMC, thanks to the superior mechanical properties of CF. These properties make this a promising material for use in aircraft brakes, rocket nozzles, engine nozzle cones, etc.

Ube Kosan has developed a Si-T-C-O fiber (Tyranno), and a completely new type of composite material (fiber-sintered ceramics) with K_{IC} values of more than
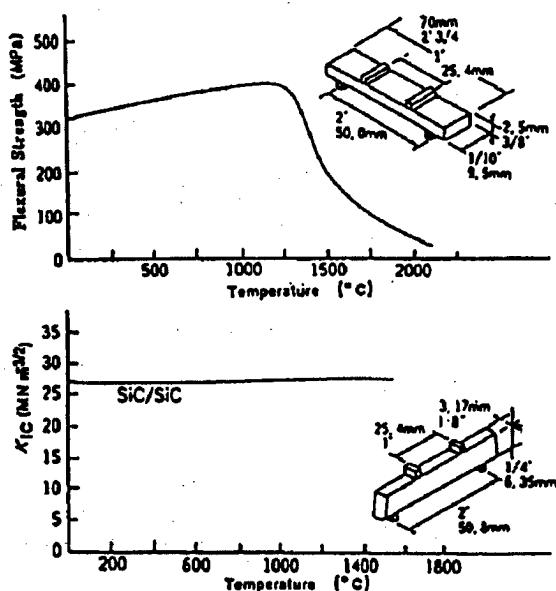
Figure 20. Characteristics of Nikalon/SiC CMC
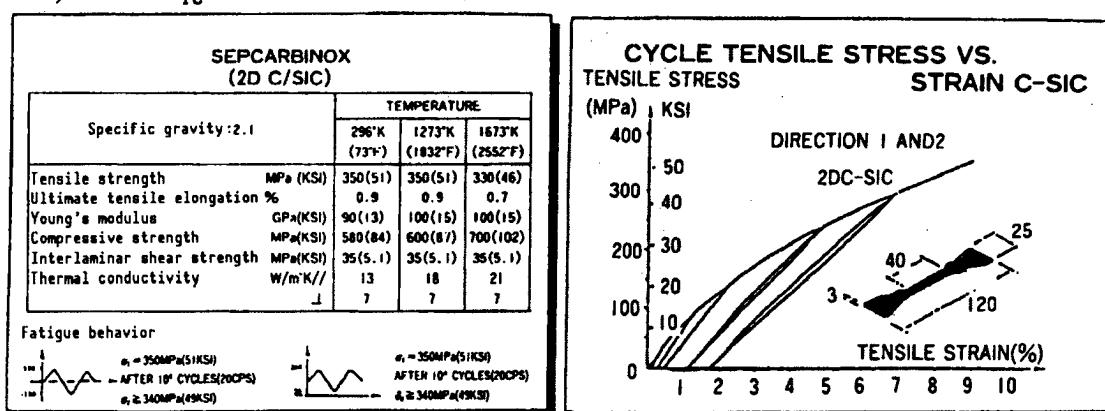
Figure 21. Characteristics of Carbon Fiber/SiC Composite Material

15 MPa·m$^{1/2}$ by hot pressing unidirectional laminated sheets. This Tyranno fiber-sintered ceramic (Tyrannohex) is, as shown in Figure 22, a hexagonally transformed fiber with very compact packing.[37] Figure 23 shows the bending strength of Tyrannohex at high temperatures.[38] This material displays high strength at the high temperature of 1,670 K in air. It is believed that this is a promising material for use at high temperatures in a wide range of applications.

(3) Whisker-Reinforced CMC

The composition process can be greatly simplified, because whiskers can be handled like powders. Moreover, the material can be isotropically strengthened, which is not possible with long fibers. Developing this material for use
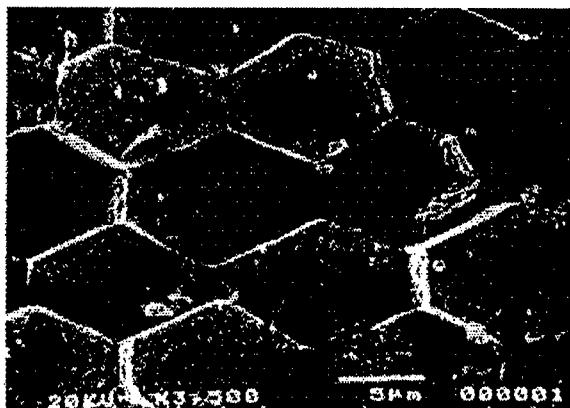
Figure 22. Fracture Cross Section of Tyrannohex

Figure 23. Bending Strengths of Tyrannohex Fabricated From Various Tyranno Fibers

in diverse fields has been considered. Of these, the most typical CMC materials are SiC whisker/alumina base, SiC whisker/zirconia base, SiC whisker/alumina/zirconia base, SiC whisker/SiC base, β–Si_3N_4 whisker/α–SiAlON base, etc. Significant improvements in the K_{IC} values of 5~8 $MPa \cdot m^{1/2}$ were not observed in whisker–reinforced CMC made of superior heat–resistant SiC unit ceramic and a Si_3N_4 matrix, which has superior mechanical properties.

The K_{IC} values were large: 12~14 $MPa \cdot m^{1/2}$ for CMCs with matrixes like zirconia or zirconia–alumina, unlike other matrixes. They also displayed superior strength, and, as shown in Figure 16, zirconia or alumina alone has the disadvantage of not being able to maintain these strengths at temperatures above 1,270 K.

The ceramics were reinforced with whiskers to reduce their brittleness, but the actual situation is that no significant progress has been made in increasing its K_{IC} values through the addition of SiC or Si_3N_4, which are considered promising high–temperature materials for use in the space and aeronautical sector.

6. Carbon Fiber/Carbon Composite Material[5]

A C/C composite material has carbon as the matrix, and is reinforced by carbon fibers. Consequently, it has superior thermal shock resistance, abrasion resistance, friction resistance, thermal

Figure 24. Relationship Between Specific Strength and Specific Rigidity of C/C Composite Materials and Other Materials

and electric conductivity, as well as high specific strengths and specific rigidity, even at high temperatures, as illustrated in Figure 24.[5]

It was these qualities that prompted the United States to begin research in the 1960s on the use of C/C composites as heat-resistant materials in nozzle cones and for the leading edges of the space shuttle. The RCC (reinforced carbon carbon) in early space shuttles used carbon fibers (rayon) with relatively low strength and low coefficient of elasticity. In the 1970s, research on the viability of using C/C composite materials as brakes in airplanes was initiated, and these materials are now being employed in jet fighters like the F-14 and the F-15. Brakes in commercial passenger planes (B-757, B-767, A-300, A-310, etc.) recently have begun to use C/C composite materials. NASA has implemented a project to employ C/C composite materials as the main structural material in the next-generation of space planes. NASA also is sponsoring research on a new C/C composite material called ACC (advanced carbon carbon) which has higher strength and elasticity, and provides better performance.

Tensile modulus of elasticity

1 PMC
2 Heat protective material
3 Carbon/carbon material
4 Metal

(a) Structural concept, materials applied

(b) Heat insulation in A-A cross section of front fuselage
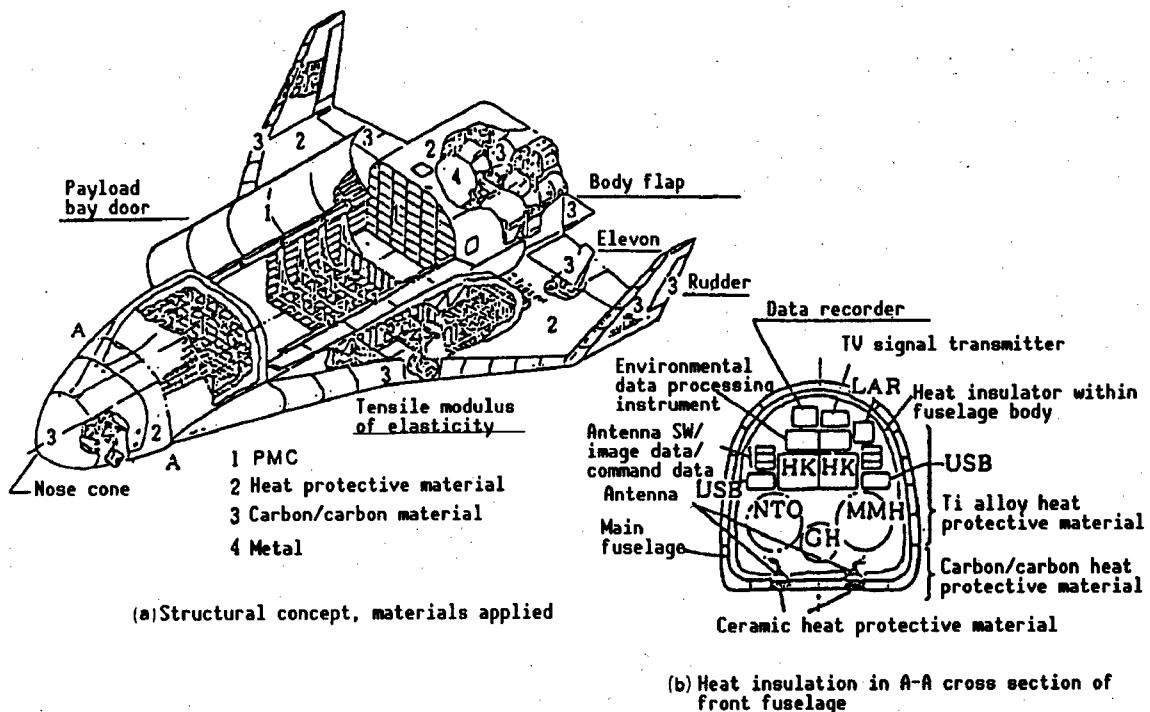
Figure 25. Application of C/C Composite Materials in HOPE Fuselage

Domestic research on C/C composite materials includes work on pitch-based carbon fibers and a PAN-based highly elastic carbon fiber. Work also is under way to improve the properties of ACC, and on possible applications of heat-resistant structural materials. The HOPE Project headed by NASDA for launching the H-II rocket is related to the development of technologies for a completely recyclable space plane. C/.C composite materials, with their high strength, elasticity, and heat resistance, are vital structural materials in this project. Figure 25 shows the heat resistance concept and the materials[39] to be applied in the HOPE Project, while Table 9 lists the target mechanical

Table 9. Target Mechanical Properties for ACC Developed by NASDA

Item		Target value
Tensile strength	kgf/mm^2	> 30
Tensile modulus of elasticity	kgf/mm^2	> 13,000
Bending strength	kgf/mm^2	> 25
Bending modulus of elasticity	kgf/mm^2	> 8,000
Fabricated dimension	mm	300^W x 300^1 x 1.5^t

values[40] for the C/C composite materials in the HOPE Project. Further, the "Development of Super Environmentally-Resistant Advanced Materials" under the Jisedai Project begun in 1989 has concentrated on the development of carbon fibers with superior heat and oxidation resistance as well as next-generation ACC featuring high strength, rigidity, and oxidation resistance at high temperatures.[41] The carbon fibers employed in C/C composite materials are PAN, pitch, or rayon. The rayon-based fiber is a commonly used fiber with a strength of 1,000 MPa and a modulus of elasticity of about 100 GPa. Thus, ACC developments concentrated on PAN-based

Figure 26. Relationship Between Tensile Strength and Modulus of Elasticity in Carbon Fibers

and pitch-based fibers. Figure 26[5] shows the strength and modulus of elasticity of PAN-based and pitch-based fibers. Fibers were classified as HT (high tensile strength), UHT (ultrahigh strength), HM (high modulus of elasticity), and UHM (ultrahigh) types. PAN-based carbon fibers are of the HT type, while pitch-based carbon fibers are a superior HM type. The pitch-based fiber is generally more oxidation resistant than the PAN-based type. Its strength and elasticity can be easily expressed when employed as a C/C composite material because it has a high coefficient of elasticity. However, it is disadvantageous in that it has low rupture elongation, is difficult to handle, and has a low compressive strength.

The matrixes employed in C/C composite materials are either thermosetting resins or thermoplasticizing resins, as shown in Table 10.[5] The main thermosetting resins are phenol, furan, and epoxy resins. These resins are easier to work than thermoplasticizing resins. CFRP technologies also can be employed. However, the carbon yield in these resins is low (less than 55 percent), while their density will increase only after several repetitions of the infiltration and carbonification processes. Pitch is a typical thermoplasticizing resin.

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Table 10. List of Ingredients for C/C Composite Materials

Carbon fibers	Matrix types	Infiltrated and densified materials

•PAN fibers/
  High elasticity
    type
  High tensile
    strength type
•Pitch fibers
  High elasticity
    type (petroleum,
    carbon type)
•Rayon fibers
	•Thermosetting resins:
	  Phenol resin
	  Furan resin
	  Epoxy resin
	  Polyimide resin
	  COPNA resin
	•Thermoplasticizing resins:
	  Pitch—Isotropic
	        —Anisotropic
	  Pitch + phenol resins
	  Aromatic polymers
	•Reinforcement materials:
	  Cokes
	  Carbon black
	  Natural graphite
	  Meso carbon
		•Thermosetting and
		thermoplasticizing
		resins:
		  Phenol resin
		  Furan resin
		  Pitch
		•CVD ingredients:
		  Methane
		  Propane
		  Benzene
		  Dichloroethylene

Pitch is easy to handle, has a relatively low softening point, and is isotropic. Mesophase pitch has also been used recently. The advantage of using pitch is that the carbonification yield is high (50~80 percent, and the oxidation resistance of the matrix carbon produced is better than that from the thermosetting resin.

The most common method for preventing the oxidation of C/C composite materials is to coat it with SiC and then crack seal it with a glass such as SiO_2. There also are reports on other methods, such as combinations of single or multiple coatings with HfC, SiC, ZrC, etc., by the chemical vapor deposition (CVD) method, and crack sealing or thick coating with SiC or Si_3N_4. These are then heated to 1,970~2,070 K. Current research efforts are focused primarily on heating to 2,070 K, and, to date, there are as yet no reports on oxidation resistance above 2,070 K.

7. Functional Gradient Materials (FGM)[12]

A very large temperature difference can occur between a heated surface and the opposite side of a piece of material, thereby creating a large thermal strain. Under such severe conditions, applying a ceramic material on the high-temperature side creates a heat-resistant layer, while a metal or a ceramic material, with a high thermal conductivity and strength on the cold side contributes greatly to the development of an FGM. The structure and percentage of airholes between the two sides are controlled such that the thermal strain is actively neutralized. The ideal concept for the structure of this material is illustrated in Figure 27.[12] Today, many researchers are exploring bases like TiC–SiC, C–SiC, ZrO_2–NiCr, TiB_2–Ni, TiB_2–Cu, etc. Properties like heat

insulation, thermal shock impact, thermal fatigue, and thermal strain reduction effectiveness are in the process of being recorded.

8. Conclusion

The temperatures that the various materials described in this article can withstand are summarized in Figure 28. The areas with slant lines represent those materials that already have been developed, while the dotted areas show those materials that will be achieved around the year 2000 as projected from current technical trends.
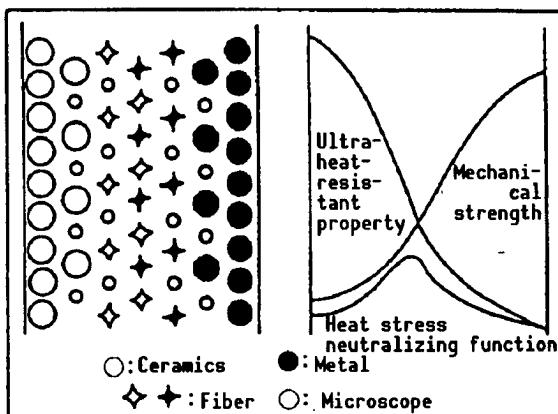
Figure 27. Depiction of Gradient Functions
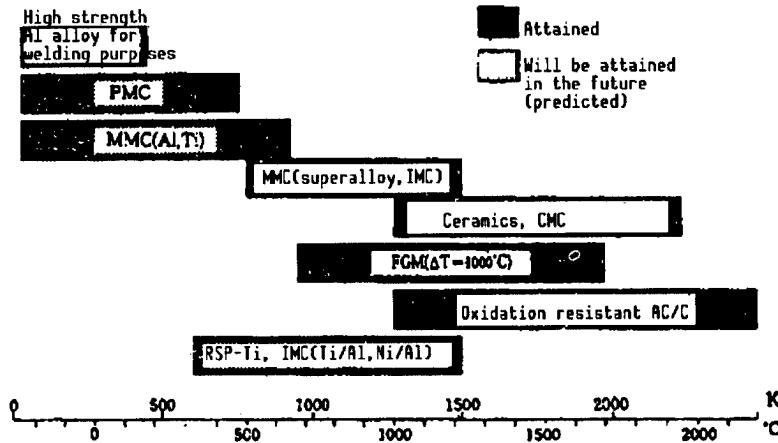
Figure 28. Temperatures That Various Materials Can Withstand

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Advanced Materials for Automobiles

[Article by Masa Yamabe, Toshio Akimune, and Masahiko Shiota, senior researchers, Materials Laboratory, Central Research Center, Nissan Motors]

[Text] 1. Introduction

It is not an exaggeration to say that this is the time for the automobile industry to take the initiative in developing solutions to the earth's environmental problems. In other words, the philosophy of the last quarter century of developing automobile hardware must now take a new turn and change to the development of "earth-friendly technologies." These include improvements in fuel consumption, exhaust control measures, recycling, safety, and preventive measures. These tasks must be given more careful consideration than ever. Naturally, one of the main themes to be tackled will be the use of advanced materials and new fabrication methods. However, not many automobile parts are made of advanced materials, because of the variety, durability, reliability, and cost of the parts. Consequently, the situation now is that automobile manufacturers have come to recognize the need for such measures, and are stepping up their research and development efforts in the areas of material design, parts design, and parts assessment technologies. In this article, we will describe four-dimensional trends for three types of materials: metallic-based, high polymer-based, and ceramic-based.

2. Research and Development Trends in Advanced Metallic Materials

It can be said that the automobile industry incorporates all kinds of technologies.

A major R&D task for virtually every automobile manufacturer is that of improving fuel consumption. In that regard, lightweight materials such as aluminum alloy, titanium alloy, or magnesium alloy are some of the materials defined as advanced materials that the alloy automobile industry can adopt in their efforts to reach this goal. We will classify these advanced metallic materials and describe the current status of research in this area.

2.1 Advanced Metallic Materials Classified According to Functions and Characteristics

Table 1 lists those advanced metallic materials whose functions or characteristics are superior to existing types.

Table 1. Types of Advanced Metallic Material Classified According to Functions and Properties

Ultralow-temperature material	Material that supports superconductivity. Structural material for use in areas of extreme cold.	Most are existing materials.
Shape-retaining alloy	Multipurpose materials like sensors, actuators, and materials for tying.	Range of materials has increased due to clearer understanding of the principles. Various applications exist.
Magnetic material	Material for many types of electrostatic devices like sensors, actuators, etc.	Diverse research, both basic and applications are in progress.
Hydrogen absorbing policy	Materials for supporting hydrogen energy systems. Heat pump materials.	Basic research on materials and mechanisms for energy systems is being conducted.
Controlled vibration alloy	Material that absorb vibrations.	Some examples of feasible applications. Quite a number of materials that are considered feasible to develop.
Ultrastrong copper	Material that supports structures whose weight can be reduced and made more compact.	Wide range of research, both basic and applied, in progress by material manufacturers.
Superhard alloy	Superior material with antiwear and antiadhering properties.	Number of applications in wall materials and tools.
Super-plastic material	Material that renders difficult-to-work materials more plastic.	Examples of applications in prototypes, shaping of difficult-to-work materials.
Superheat resistant material	Structural material for use at extremely high temperatures.	Range of research increased materials other than metallic.
Super-conducting materials	Material for use in devices generate strong magnetic fields. High efficiency electric wires.	Expected to be a new driving source, but there will be very little connection with the automobile.

The materials that are expected to have a significant effect on the automobile industry, both qualitatively and quantitatively, are "hydrogen absorbing-storing alloys," "ultrasonic steel," and "ultraheat-resistant materials." A hydrogen-absorbing storing alloy is employed in actuators and heat pumps. Research on its effects on automobiles is being closely tracked by automobile manufacturers, particularly its use as a material for supporting the hydrogen energy system. This research is expected to revolutionize designs for the engine, fuel system, chassis layout, and the heat control system.

Ultrastrong steel is an iron-based material with a tensile strength of more than 2 GPa. Its use has helped reduce the weight of value-added parts in military, air, and space vehicles, as well as racing vehicles, thereby making the vehicles more compact. This material is expected to become a strong competitor among lightweight materials like aluminum or titanium in the design of sporty luxury cars in accordance with the present trend in tastes.

There are a number of cases where steel materials are again being recognized for their light weight.

The heat-resistant materials mentioned here are nickel, cobalt, and iron-based materials used for fabricating such automobile parts as valves, turbochargers, and other engine parts. The number of applications for these materials has been greatly expanded through cost reduction and by improving their workability, i.e., machining and ease of casting, thus creating a possible revolution in engine design. The development of new materials in recent years has spurred the use of intermetallic compounds.

2.2 Classification According to Morphology and Shape

Table 2 lists the types of advanced metallic materials classified according to their morphology and shape. The intermetallic compounds listed here display values for heat resistance, toughness, and heat conductivity that are between those of metals and ceramics. The type and characteristics of such materials cover a wide range. Consequently, their application in areas that are currently covered by ceramics is being followed closely. For example, their light weight, high performance, and compactness are expected to revolutionize the automobile industry by using them to produce heat-resistant parts in the engine like the turbocharger rotor, valve, piston or hot charger, or by using them in heat-removal and heat-resistant parts of the engine, such as parts in the turbo compound system, cam follower, cam, etc. Moreover, there are still many properties of intermetallic compounds that are unknown, and thus such compounds may affect the automobile industry in unexpected areas.

MMC (metal matrix composite) materials have attracted considerable attention since their development, but to date, they have very few applications. Problems such as cost and productivity remain to be tackled before they can be applied as a lightweight yet strong material. For example, one of the main research themes in the application of MMCs as structural materials involves their fracture mechanism and heat deformation.

Table 2. Types of Advanced Metallic Materials Classified According to Structure and Configuration

Type of material	Description	State of development
Intermetallic compound	Heat insulating material for filling gaps between ceramics metal. Possess many functions.	Examples of investigations of use of TiAl rotor in automobiles. Great expectations for aluminade.
FRM	Lightweight structural material. Material design to meet purpose is possible.	Gradual application to pistons, conrods, etc.
Amorphous	Functional material with magnetic, catalytic properties. Corrosion resistant. Durable and strength reinforced.	Already employed as magnetic material. Much basic research on it.
Ultrafine powder	Possess multiple functions like catalytic effects, magnetic, combustible, absorbs infrared rays, etc.	Great expectations for size of effects on boundary energy. Much basic research.
Foils, fibers, porous material	Material with increased hardness, corrosion resistivity, rigidness, sound absorption, and workability.	Research to meet different purposes is considered at various development levels. Several feasible applications exist.

Cast MMC with distributed particles is a low-cost, mass-produced material that has been attracting considerable attention lately.

It is equally important that not only material shapes but also shapes where high-cost materials are used in some parts of structures be considered. Thus, techniques like surface treatment for value-adding or hybridization of materials are becoming increasingly important.

2.3 Classification According to Method of Fabrication

In most cases, new fabrication methods are developed for the advanced materials described above.

Thus, new materials are developed in conjunction with new fabrication techniques, or through the application of existing techniques to materials to which they never before had been applied.

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Fabrication methods for advanced metallic materials are listed in Table 3. Most materials are not very cost effective.

Table 3. Examples of Methods for the Fabrication of New Metallic Materials

Dissolution/casting	Unidirectional solidifying and casting Rapid cooling solidifying method High pressure solidifying method Plasma dissolution method Vacuum arc dissolution method Electroslag dissolution method
Casting/press	Constant temperature casting method Controlled rolling Ausforming
Heat treatment and surface treatment	PVD CVD Ion injection Laser thermal treatment
Powder metal	CIP HIP Hot press Powder extrusion

Either the material is modified in response to production needs, or production techniques are modified to take full advantage of the material's properties before these materials can become practical. The feasible thing to do would be to develop a system whereby research and development in production techniques and materials can be conducted simultaneously.

2.4 Conclusion

Despite the problems associated with advanced metallic materials, they are still superior to other materials in terms of quality and quantity, and have fewer outstanding problems before they can be put to practical use.

Although plastics or ceramics will be used increasingly, metallic materials nonetheless will remain the principal materials employed by the automobile industry.

3. Research and Development Trends in High Polymers

High polymers were developed several decades ago in response to the need to reduce the weight of automobiles. They were developed as a replacement for metals, and, as such, had the same structure as the metal parts they were intended to replace. The only difference was in its thickness. Today, however,

weight reduction is not the only problem to be tackled. Other considerations include structural needs, like the ease of single body fabrication or structural freedom, as well as demands that take advantage of the properties of high polymers such as their viscoelasticity, energy attenuative properties, and a superior ability to retain their shape. In other words, automobile parts that take advantage of the properties of high polymer materials are now appearing on the scene. Some examples include a resin outer plate, GFRP spring, gasoline tank, various shock absorbers, and aero parts. The high polymers that have attracted a lot of attention in the last few years as a form of advanced material include thermoplasticizing resin, in particular, and polymer alloys or engineering plastics for injection or blow molding. We will describe the fundamental technologies necessary for realizing the application of resin materials, particularly polymer alloys and engineering plastics.

3.1 Applications of High Polymer Materials

There are virtually no applications of high polymer materials in automobiles that qualify as "advanced materials" in the strict sense. In the following we will describe the resin materials used in automobiles today.

3.1.1 Amount and Changes in the Use of Resin Materials

Figure 1 compares the amount of resin materials used in each model of the Cedric and Bluebird cars as they have changed over the years. In both cases, there was a significant increase in the amount of PP composite material used. Although not apparent from the diagram, another characteristic is the significant increase in the use of engineering plastics in recent years.
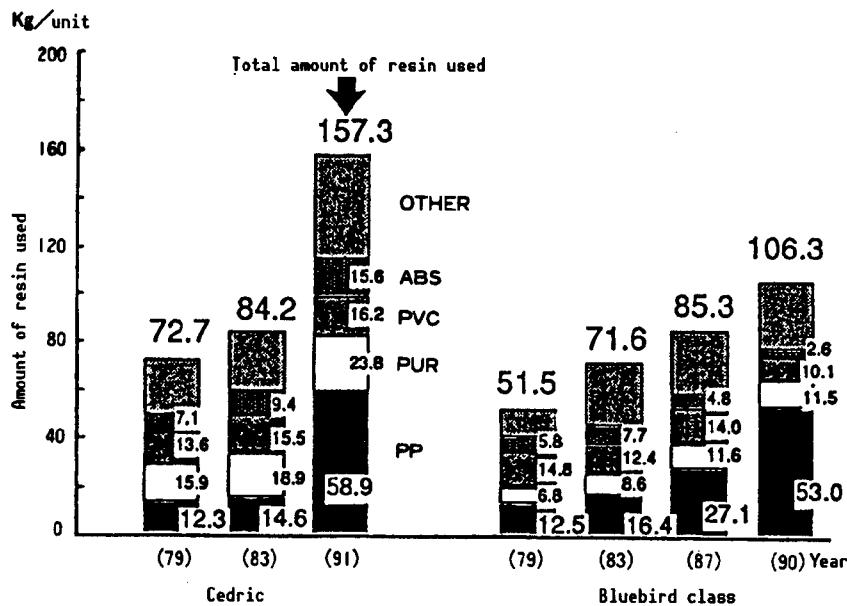
Figure 1. Transition in Amount of Resin Used

Many new materials have, in fact, evolved from PP by adding different elements in varying amounts in an effort to alter its performance (for instance, shock resistance, dimensional stability, fluidity, ease of coating, etc.). For this reason, resin materials can, in a sense, be classified as advanced materials.

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Figure 2. Resin Materials in an Automobile

3.1.2 Current Status of the Use of Resin Materials in Automobiles

Figure 2 illustrates the quantity, type, and fabrication method for materials used in a four-door sedan. Most parts are fabricated by the injection method because of its molding cycle and quality control.

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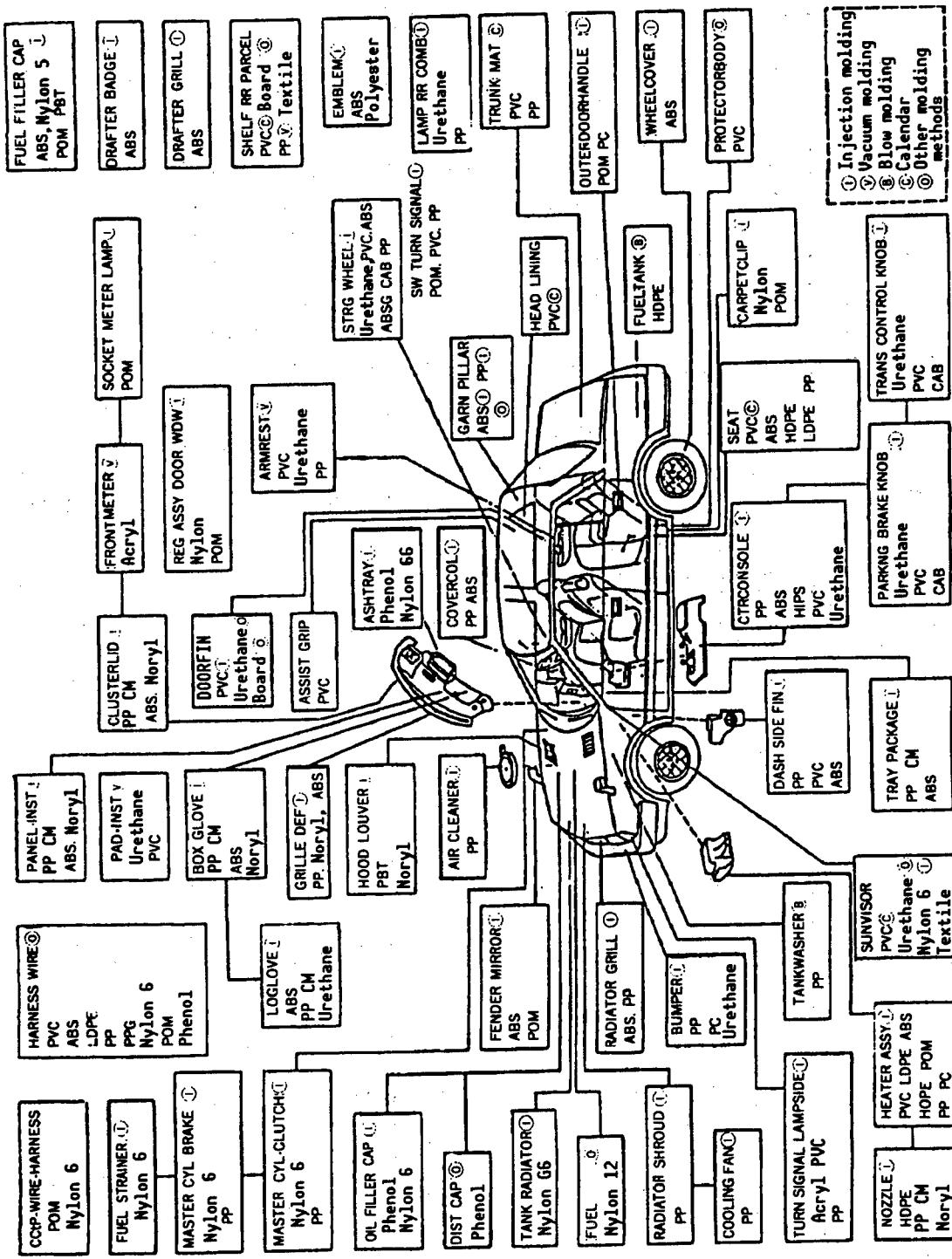
3.2 Research and Development Trends in High Polymer Materials

The following are some of the problems that require resolution before high polymer materials can be applied in automobile parts:

    1) fabrication method;
    2) material;
    3) assessment techniques; and
    4) prediction techniques.

3.2.1 Fabrication Method

Resin-based parts are becoming larger and single-bodied in recent years in response to demands from the design department. The PP material that is most frequently used has poor fluidity. Consequently, molds and molding materials must be large. In response, low-pressure molding techniques had to be developed. However, the molding cycle tends to become longer as the molding pressure decreases. The relationship between the molding pressure of each type of molding method and the molding cycle is shown in Figure 3. This relationship changes with material type and shape, but the fabrication methods deemed most promising for the automobile industry are the gas assist injection molding method, the injection press method, and the blow method. These are the fundamental molding techniques for advanced materials whose fluidity deteriorates during molding.

3.2.2 Material

We already have touched on some ways to realize low-pressure molding. Another way is to reduce the material's viscosity. However, improvements in the fluidity of the material will reduce its dimensional stability and even its rigidity.

Figure 3. Comparison of Molding Pressures
(Excerpted from Reference 1)

Polymer alloys are made by mixing several alloys together. They were developed based on the concept of overcoming the shortcomings in each constituent alloy through the addition of other constituents while enhancing their strong points. There is a need to create polymer alloys with contradicting properties, such as low coefficient of linear expansion yet low specific weight,

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high fluidity yet low cost. For this reason, alloying techniques at the molecular level must be established. This is a problem that must be solved through cooperation between automobile and material manufacturers.

Not only engineering plastics but also polymer alloys increasingly are being employed in injection and blow molding. These materials were developed primarily for use as superior transcription materials, such as outer plates, but great changes can occur in the material's transcription property depending on the mold temperature or blow pressure. Thus, developments in both the material and the method must be pursued.

3.2.3 Assessment Techniques

The environment in which the engine operates must be well understood before a resin material can be used to fabricate engine parts. For that reason, new methods that are different from conventional steel-based assessment methods must be developed. Let us take fatigue assessment as a case in point. Creep mechanism, stress neutralization, and both mechanical and thermal fatigue must be considered. However, much time and effort is required to conduct fatigue tests for all kinds of conditions. Consequently, there is an urgent need to gain a theoretical understanding of the fatigue mechanism in various materials and to work out an appropriate formula.

3.2.4 Prediction Techniques

Analysis and subdynamic analysis of large deformations in high polymers, as well as analysis of the parts production process (for example, fluid flow analysis) can be achieved today as a result of recent improvements in computing technologies. Slowly but gradually, for the design of both conventional parts and those made of advanced materials, process design and ways to predict the characteristics of parts made by these processes are being established. Figure 4 is a packing analysis diagram of a PPO/PA alloy front fender during injection molding. In injection molding, the number of gates, the shape and position, and the injection temperature and pressure have to be altered according to the type of material used. As a result, much time and effort has to be expended before this method can be applied to the fabrication of new materials. In this example, the time required for the development of a new material was greatly reduced through an investigation of its characteristics followed by an analysis of its process based on its flow pattern.

Figure 4. Analytical Packing Diagram for Injection-Molded Structure

Figure 5 shows an analytical example of the predicted distortions resulting from a difference in the linear expansion of steel and the resin-based front fender when it was coated while it was being molded. In this manner, the

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suitability of methods for attaching parts to the automobile can be investigated on the table before they are actually used.

3.3 Conclusion

As described above, high polymer materials are considered to have promise for use in the automobile industry in applications that take full advantage of their properties. High polymers no longer are merely replacements for conventional steel. As such, there is an urgent need for new fundamental technologies such as fabrication methods,

Figure 5. Analytical Diagram of Thermal Distortion

assessment techniques, or even prediction techniques to be established. Moreover, automobile, material, and machine manufacturers must cooperate in efforts to develop effective ways of fabricating, employing, and recycling advanced high polymer materials as a means of improving the earth's environment.

4. Research and Development Trends in Ceramic Materials

Like metals and high polymers, ceramics have a long history, but they have only a limited range of industrial applications because of their brittleness. Significant improvements in ceramics over the past 10 years have, however, helped increase the number of uses for ceramics in machine parts, and now ceramics are widely employed in fuel conservation-type automobile engines[2-6] (Table 4). All ceramics applications take advantage of the material's light weight, high strength, heat resistance, and friction resistance. Unfortunately, only a few engine parts are made of ceramics. This is because the mechanical reliability of ceramics is still questionable, and also because ceramics are relatively more expensive than their metal counterparts.

Table 4. Ceramics Developed for Applications in Engine Parts

Engine part	Ceramic material	Properties employed	Effects	Application realized
Glow plug	Silicon nitride	Acid corrosion resistant	Improved engine starting	1981
Hot plug	Silicon nitride	Heat resistant and adiabatic	Improved fuel consumption	1983
Locker arm pad	Silicon nitride	Antiwear	Reduced vibrations	1984
Turbo charger rotor	Silicon nitride	Lightweight and heat resistant	Improved response	1985
Port liner	Silicon nitride	Adiabatic	Improved catalytic effects	1985

Although ceramics are receiving much support as a resource conserving material, people are still hesitant to fully employ them because of their low reliability and high cost as compared to metals. The state-of-the-art in ceramic technology and future problems must be well understood before ceramic structural parts can be fully employed.

4.1 Examples of the Application of Ceramics in Structures

4.1.1 Automobile Parts (Table 4)

The automobile parts shown in Table 4 are made primarily of high-strength, heat- and corrosion-resistant silicon nitride. The ceramic material used is primarily nonoxidizing silicon nitride with average values for strength, brittleness, and hardness. In particular, the turbocharger rotor takes advantage of the lightweight and heat-resistant features of ceramics and contributes to an improvement of the overall characteristics of the engine. Other factors can be attributed to other engine parts. The heat-insulation property of aluminum titanate also is currently drawing a lot of attention. Highly brittle zirconia, meanwhile, is not employed because of its weight, which is almost equal to that of metals, and its drop in strength at high temperatures. Thus, it does not contribute to an improvement in the engine.

4.1.2 Industrial Machine parts (Table 5)

Industrial machine parts do not imply only strong parts, like in press machines, but also include applications in cutting tools, bearings, and mechanical seals.[7-10] Some unique applications also have been reported, for example, in making holes in steel plates for positioning robot welders in automobile assembly lines. The characteristics of ceramics are fully exploited when applied to industrial equipment, but application methods and configurations must be optimized, and durability must be improved to a level that is compatible with that of metals.

Table 5. Examples of Ceramics Applications in Industrial Machine Parts

Tool	Ceramic material	Properties employed
Bite	Alumina/SiC-whisker/ alumina	Anticorrosion property
Locate	Zirconia Silicon nitride	Anticorrosion property High rigidity
Punch	Zirconia	High rigidity/anticorrosion property
Bearing	Silicon nitride	Anticorrosion property
Welding torch	Silicon nitride/silicon carbide	Heat and corrosion resistant

4.2 Problems With Ceramic Parts

4.2.2 Reliability

Historically speaking, design technologies have been based on research on fracture mechanisms and materials. Ceramics have such a wide range of strengths that conventional metallic material technologies cannot be directly applied. Instead, they must be selected through reliable tests. Mechanical characteristics, such as shock and fatigue mechanisms, have not been analyzed yet, and there is an urgent need to gather basic data. Also, it is necessary to be able to guarantee strength through nondestructive testing.

4.2.2 Cost

Not only the particular characteristics of ceramics but also production cost must be considered when developing production techniques. One of the reasons for the difficulty in producing ceramics for the general public is their high unit cost as compared to metals. This is because shape molding, sintering, and other techniques are a vital part of their production process. Low-cost technologies, meanwhile, are improving. The new DIMOXTM process currently being developed in the United States is attracting a lot of attention as a low-cost manufacturing process for ceramics. In this process, the aluminum is oxidized directly.

4.3 Problems Facing Ceramics in Structural Applications

The development of future ceramics technologies will focus on nationally funded projects aimed at developing electric generators or ceramic gas turbines for use in automobiles. It also includes the development of solid electrolytes for use in fuel batteries or sodium sulphite batteries. Next, let us describe the ceramic parts and characteristic material values targeted in these projects (Table 6).

Table 6. Future Driving Machines and the Materials of Which They Are Made

Driving machines and their application	Ceramics employed
Ceramic gas turbine	Silicon nitride and silicon carbide
Fuel battery	Stabilized zirconia Lithium aluminate Oxidized nickel
Sodium-sulphur battery	β alumina

4.3.1 Ceramic Gas Turbine

In Japan, the development of a ceramic gas turbine (100 kW) for use in automobiles is under way as part of a government project headed by the Ministry of International Trade and Industry.[11] In the United States, a similar project called the ATTAP (Advanced Turbine Technology Application Project) is focusing on material and part compatibility technology. Gas turbine parts are used under very severe conditions: over 1,350°C in an oxidizing atmosphere. For this reason, the characteristics of ceramics are fully exploited in material and manufacturing process development. The principal materials employed are silicon nitride and silicon carbide. The ceramics used in gas turbines are still being monitored for possible effects such as corrosion by fuel gas, thermal impact due to fuel flow hindrance, and particle impact by the approaching oxidation scale.

4.3.2 Solid Electrolyte for Use in Fuel or Na-S Batteries[13,14]

Research is being actively pursued on the use of stabilized zirconia or β alumina as the solid electrolyte in fuel batteries or Na-S batteries, respectively. The former battery requires a temperature of more than 800°C for electrode reaction, while for the latter the temperature must be more than 300°C. The mechanical and electrical stability of ceramics under these conditions are important to prevent high-temperature corrosion. Using ceramics in automobiles can lead to problems such as difficulty in restarting the engine after it has not been run for a long period, or poor resistance to vibrations when the automobile is being driven.

4.4 Summary

The performance level of ceramics intended for structural use is very severe, and much time and effort almost certainly will be required to achieve them. Ceramics will not simply serve as replacements for metals, and, therefore, will require definite application techniques. It is hoped that those characteristics unique to ceramics and unavailable in metals can be fully employed by gradually overcoming all problems so that in the future ceramics will become leading materials.

5. Conclusion

The advanced materials deemed important to the automobile industry are many compared to those adopted by the space and aeronautical, or the leisure industries. Nonetheless, actual applications are comparatively few. There are also very few reports of advanced materials being employed in automobiles. This can be attributed to cost (it is necessary for cost per unit weight to be kept as low as possible) and the production process (large quantities of parts with complicated shapes must be produced). In recent years, "earth-friendly" has become another important factor to consider when developing automobiles or materials. For this reason, big problems in the use of advanced materials, such as recycling, fiber reinforcement, and environmental problems, are being addressed. Thus, it is difficult for a completely unknown material to appear suddenly and to dominate the automobile industry market. It is believed that

an advanced material developer must first endeavor to modify the advanced material in front of him or her. Thus, those materials deemed useless at this point in time should not be completely ignored. Rather, they should be assessed from other aspects, and basic research should be redone while predicting environmental and social needs 20 years ahead.

Cooperative efforts between researchers and production lines will become more and more important. Relationships between materials and automobile manufacturers will become closer and more important, not only for cost and material supply, but also in areas like recycling, research and development, etc.

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Management, Recycling of Plastic Waste

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[Article by Kazuhiro Nakane, director, PR and Investigations, Association To
Promote Plastic Waste Management]

[Text] 1. Plastic Waste and Garbage Problem

The Association To Promote Plastic Waste Management (hereafter termed the
Association) was established in November 1971. Thus, today it is about 20
years old. At the time of its establishment, plastic packaging was said to be
the major culprit in the garbage problem, and our forebears met with a
multitude of problems when trying to solve it.

Table 1. Status of Waste Treatment in Japan

Year	Population in treatment area (million people)	Total population ratio (%)	Total weight discharged (1,000 t/day)	Incinerated weight (1,000 t/day)	Incinerating ratio (%)
1960	47.4	49.8	24.4	7.6	31.1
1965	64.2	65.4	44.5	16.9	37.9
1970	84.7	81.6	77.0	42.6	55.3
1975	111.6	99.3	87.2	50.4	57.8
1980	116.7	99.4	113.7	68.7	60.4
1985	120.8	99.6	113.8	80.3	70.6
1986	121.8	99.8	117.7	84.5	71.9
1987	122.0	99.9	122.8	89.1	72.6
1988	122.6	99.9	128.6	93.6	72.8

As is evident from Table 3, domestic plastic consumption leaped 7.5 times from
the 1960s to the 1970s. Most of this consumption was in the form of plastic
packaging materials and disposable containers (Table 4).

Table 2. Waste Incineration in Japan, United States, and Europe (1986)

Country	Population (million people)	General waste (10,000 t/year)	Number of incinerators	Incinerating ratio (%)	Exhaust gas treatment (%)
Japan	122	4,296	1,899	72	100
United States	232	13,690	157	10	15
Austria	6	160	3	22	33
Belgium	10	280	29	47	38
Switzerland	6	220	334	77	18
West Germany	60	1,900	47	34	66
Denmark	5	180	46	81	0
France	54	1,700	284	41	0
England	57	1,800	38	10	0
Italy	57	1,400	80	18	4
Netherlands	14	430	11	40	9
Sweden	8	250	23	56	22
Total Europe	277	8,320	595	31	10

Note: According to surveys in 1990 in Europe and the United States, the
incinerating ratio in the United States is 14 percent and the average in
Europe is 33 percent. Exhaust gas treatment ratio in Europe is higher
than that indicated in the table.

Table 3. Production of Plastics and Discharge Weight (1,000 t/year)

Year	Production weight	Domestic consumption	Total weight discharged	General wastes	Industrial wastes
1960	554	545			
1965	1,601	1,373			
1970	5,127	4,080			
1974	6,693	5,828	2,532	1,478	1,054
1975	5,167	3,986	2,613	1,471	1,142
1979	8,210	7,256	2,853	1,545	1,308
1980	7,518	6,700	3,258	1,784	1,474
1985	9,232	8,272	4,188	2,317	1,871
1986	9,374	8,321	4,528	2,502	2,026
1987	10,032	8,844	4,656	2,604	2,052
1988	11,016	9,969	4,878	2,761	2,117
1989	11,912	10,944	5,060	2,911	2,149

Table 4. Comparison of Various Statistics

	Unit	1960	1970	Comparison
Domestic plastic consumption	1,000 t/yr	545	4,085	times 7.5
Population ratio within treatment area	%	49.8	81.6	—
Discharge volume of general waste	1,000 t/day	24.4	77.0	3.2
Amount of incinerated waste	1,000 t/day	7.6	42.6	5.6
Ratio of waste incinerated	%	31.1	55.3	—
Waste calorific value for Osaka city	kcal/kg	1,095	1,138	1.04

In 1969, the Osaka Expo Committee's decision not to use plastic containers because of the disposal problem, and the National Garbage Disposal Committee's ultimatum to the nation to establish plastic waste management measures and to suppress the use of plastic containers rocked the plastic industry.

In spite of that, garbage volume has increased 3.2 times over the past 10 years. The chief reason is the population flow from the rural areas to the cities, thereby raising the garbage volume to total population ratio within a garbage treatment area to 81.6 percent in 1970 (Table 1). According to the garbage statistics of Osaka city, calorific value during this period increased only by about 1.04 times, and, in fact, increase in the garbage volume represented a bigger burden to the incinerating facilities in the local autonomous areas. In spite of efforts taken by the Ministry of Health and Public Cleaning Bodies in autonomous areas to increase and improve existing incinerating facilities, they are still insufficient given the 5.6 increase in garbage volume during the period from 1960 to 1970, despite the fact that the garbage ratio remained stagnant at 55 percent.

2. Establishment of Association To Promote Plastic Waste Management and Technology Development During Its Early Stages

Members of the plastics industry gathered to form the Association To Promote Plastic Waste Management in November 1971 to take over the work and technical developments previously undertaken by the Petrochemical Industrial Association and the Polyvinyl Industrial Association. The technologies and cities that have cooperated with the Association to date, are as follows:

- Recycling techniques in the form of crushing, cleaning, melting, and solidifying (Funabashi city, 1972 ~)

- Incinerating tests in special furnace (Koshigawa city, 1973 ~)

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- Thermal decomposition test (Kusatsu city, 1973 ~)

- Nurturing recycling industry (liabilities guarantee, technology development, products introduction, etc.)

- Various surveys

- PR activities (publication of periodicals, movies/videos, exhibitions, etc.)

There are still many people who believe that recycling means a change in the product's shape. As a result, this Association has developed recycling techniques in the form of dissolution and solidification methods.

With the cooperation of the Funabashi city government, plastic waste was collected from each household in the city and then turned into flat sheets or pellets after being "crushed," "cleaned," "dehydrated," and then "extruded" at the experimental facilities. Some of the problems discovered in this process are as follows:

- Extremely high cost
- Product shape (product foamed and released bad smells), and product could not be marketed
- Plastic waste separately collected from households required further selection before recycling

Quite a number of people were also of the opinion that if plastic waste could not be recycled in new shapes, then it should at least be recycled into its original raw petroleum material. Therefore, thermal decomposition experiments were performed with the cooperation of Kusatsu city. Process features and the research bodies that cooperated are:

- Sanyo Electric, two-step thermal decomposition by microwave heating, melting, and screwing method.

- Mitsubishi Heavy Industries, two-step thermal decomposition by melting and reflux redecomposition of products with high boiling points.

- Sumitomo Heavy Industries, fluid bed method, treatment by mixing oil waste and rubber waste with plastic waste.

Technically speaking, all the above techniques were plausible, and fuel oil recovery was indeed possible. However, these remained at the experimental stage because of the high cost required and difficulties in collecting huge amounts of pure plastic waste.

The quality of the products resulting from these recycling techniques were so bad that no market could be found for them. As a result of these observations, the Association has thus decided not to separate garbage for collecting and has proposed incineration of the mixed garbage.

In spite of the negative results of this experiment, this world's first attempt to recycle plastic waste through separate collection has sent strong reverberations throughout the plastic waste recycling world. Visitors to the facilities have deepened their knowledge on the plastic waste problem and recycling techniques.

3. Revision of Air Pollution Prevention Law and Plastic Waste Management

Revision of the Air Pollution Prevention Law in 1977 reduced the concentration of hydrogen chloride released from garbage incinerators to 430 ppm. Existing incinerators had to comply as of 1979. Small- and medium-size incinerators were asked by the Ministry of Health to separate their plastic waste before burning in case of difficulties in establishing exhaust gas treatment facilities.

In the past, plastic waste released toxic gas when burned. Most incinerator operators then refused to treat plastic waste because of the belief that the released gas would damage the incinerators. There were even cases of mutual understandings between incinerator operators and local citizens that plastic waste would not be burned when new incinerators were constructed.

The designed calorific value (minimum heat generated) in incinerators constructed before 1970 was below 1,500 kcal/kg. Today, however, the garbage treatment capabilities of these incinerators have dropped due to an increase in the calorific vale of city garbage. This is due in turn to a drop in the water and ash content, and an increase in paper and plastic garbage. Thus, the trend today is to remove the plastic waste with high calorific value from other garbage before incinerating. In particular, movements to collect plastic waste separately and dump them in landfills were implemented in the Tokyo Metropolitan area, and this has spread throughout the nation. The results of a survey by the Ministry of Health in 1982 (although slightly old statistics) showed that about half of the local autonomous governing bodies had designated plastic waste as difficult to dispose (meaning that it is difficult to treat them at the incinerating facilities managed by the autonomous bodies) and as such were collected separately and dumped as landfills.

According to the results of a survey recently conducted by this Association, of the 11 cities in Japan, the Tokyo metropolitan area, Nagoya city, and Hiroshima city have designed plastic waste as "difficult to dispose," and as such are collecting them separately from other garbage (citizens separate the garbage and as such only half the total work is necessary), and are dumping them at landfills. Meanwhile, the cities of Sapporo, Sendai, Kawasaki, Yokohama, Kyoto, Osaka, Kobe, Kita, Kyushu, and Fukuoka are collecting plastic waste as combustible garbage and are actually incinerating them. Surveys of other cities have proved that disposal of plastic waste depends on whether the city has a landfill or not, and on the citizens' awareness.

Quite a number of cities do not incinerate their plastic waste due to citizen pressure, but of these about 20~30 suffer from a lack of landfills and/or administrative problems in the collection of separated plastic wastes, melting, solidification and, then reducing its melting point before dumping into landfills.

4. Introduction of Modern Incinerating Facilities and Improvement of Incinerating Capacity, Treatment Status in United States and Europe

The Ministry of Health has increased its budget for garbage treatment facilities. Since 1978, the garbage treatment budget has increased annually by ¥50 billion. This and the efforts of Autonomous Public Cleaning Bodies have, each year, raised the incinerating ratio and calorific value such that in 1988, the incinerating ratio achieved was 72.8 percent.

Currently, incinerators are usually constructed with a designed calorific value of around 3,000 kcal/kg, and are equipped with incinerating temperature control, measures to prevent the generation of clinkers (the flyash that melts and sticks to the walls of incinerators at high temperatures), and facilities to treat exhaust gas. As a result, plastic waste can be incinerated easily. However, about a third of the 2,000~2,200 kcal/kg-class incinerators constructed before 1975 still remain, and until they are upgraded toxic gases will be generated when plastic waste is incinerated in them. The unpopularity of plastic waste will continue unless the misconception by the general population that incineration of plastic waste will damage incinerators is erased. Table 2 compares the incinerators in Japan with those in the United States and Europe. Although there are countries like Switzerland and Denmark with high incinerating ratios, the most common method for plastic waste disposal throughout the world is still landfilling.

Plastic waste in the United States was, until recently, treated by the sanitary landfill method, where waste was simply dumped into holes in the ground and then covered up. The cost of this procedure is low at $5~10/ton. However, contamination of underground water and the release of toxic methane gas have forced these landfills to be regulated or closed, thereby rapidly decreasing the number of landfills available for dumping. In particular, landfills in the east coast area and around the Great Lakes area have decreased such that some garbage trucks or ships have to travel more than 1,000 km to the south or central United States to dump, thereby causing costs to jump to $100/t to $150/t.

Moreover, most incinerating facilities in the United States usually are privately owned, and costs are the most important factor in their management. This is unlike Japanese incinerators, which are publicly owned, such that the heat generated in the incinerators can be channeled to heat public amenities like pools. In fact, NIMBY (Not In My Back Yard) movements are very strong in the United States.

5. Conservation Conditions and Plastic Waste Collection by Autonomous Bodies

The collection of used materials will not lead to conservation at all. The following conditions must be satisfied for conservation:

Collection: Recyclable waste must be collected in large quantities. Citizens separate recyclable waste, which is collected by an agent commissioned by the administrative body.

Selection: Agent commissioned by administrative body separates bottles, cans, papers, etc., before sending them off to the recycler.

Recycling: Used as raw materials by paper makers, bottlers, iron and steel makers, etc.

Market: Widely used as high quality, cost effective product.

The many types of plastic waste (there are about 10 different types of plastic waste from city garbage alone), the usually dirty food containers or packaging materials, the less than 10 g weight per plastic container, and the extreme difficulty in separating the same plastic material from the city's garbage are typical problems faced by the industry today. The only plastic waste that can be collected in sizable amounts would probably be the easy-to-wash PET beverage bottles (about 50 g) and some PS foam products. Another very important condition is the ease of recognizing the different products by the general public.

Let us next compare recycling of plastic waste with used paper, empty bottles, and cans, which are being recycled already. Used papers include newspapers, magazines, and cardboard paper, but do not include paper used for wrapping foods. Empty bottles and cans can be easily purified by heating and melting at high temperatures, since organic substances like food will be burned up.

In the 1980s, 25 cities including, Mito, Hitachi, Fuchu, Kunitachi, Kamakura, Kusatsu, Himeji, Matsue, and Matsuyama, began collecting foam PS products and containers. Unfortunately, this campaign was canceled after a relatively short time as a result of the poor quality (same material, degree of stains or dirt) and quantity of the plastic waste recovered from the garbage as well as the absence of a market for the recycled products. Only Kusatsu city, with the citizens' consent, is still collecting plastic waste to be recycled into flower pots, etc. Reports indicate, however, that costs are extremely high.

6. Recycling Promotion Law, Revision of Waste Cleaning Law, and Response From Plastic Industries

In December 1990, the Livelihood Environment Committee called for another conference to revise the Haisoho (Waste Cleaning Law), which was revised in 1975, and by October 1991 proposals had been drafted. At the same time, the Ministry of International Trade and Industry (MITI) called for industrial subconferences on waste management and recycling in December 1990, and established the Law To Promote Recycling of Resources in April 1991. The plastic-resin industry made the following proposals as a result of deliberations by the waste management and recycling subcommittees:

- Recyclable substances should be recycled to the extent possible.

- Substances that are difficult to recycle should be incinerated, and the energy released should be recovered.

- Products should be made thinner and more durable.

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Meanwhile, plastic producers formed liaison committees to investigate waste to reduce packaging waste and to promote recycling.

These investigations were then fed back to the Industrial Committee on Waste Management and the Subcommittee for Recycling to produce the following guidelines:

(1) Measures to promote recycling and product use without processing

    1) Execution of model recycling of PET beverage bottles.

    2) Promotion of styrofoam packaging materials for fish, electrical home appliances, etc.

    3) Improve recovery rate of polyvinyl films used in agriculture industry (from 38~50 percent).

    4) Recovery of styrofoam trays for distribution and execution of model recycling program.

(2) Measures to promote energy recovery and use; measures to promote the recovery and use of difficult to dispose of materials without further processing

    • Recovery and use of energy through appropriate incineration techniques.

(3) Promotion of lighter, thinner, and more durable products

In response to these guidelines, the plastic products industries have instituted the following measures:

    1) The PET Bottle Council, in collaboration with Yamaichi Garet, plans to construct in 1992 a factory to collect 5,000 tons of PET bottles per year from the north Kanto area.

    2) The Styrofoam Recycling Association will promote the recycling of fish boxes and shock absorbers for packaging electrical home appliances.

    3) The Polystyrene Sheets Industrial Association will promote the recovery of foam PS trays and equip recycling factories in Kanto and kansai area. Also, foam PS tray recycling programs are being implemented by major tray makers and stores with large sales volumes.

    4) The Plastic Waste Management Promotion Association has increased its staff and budget, and enlarged its membership to strengthen its activities.

7. Recycling and Industrial Plastic Waste

There are a great many types of industrial plastic waste. These include plastic scraps that are created during the manufacturing, processing, or assembling processes of plastic products; defective products; and the packaging materials used for transporting various products or materials. Their applications are distinct. The cleaned waste can be recycled into pellets for use as a cheap raw material. It is estimated that recycled production will reach about 490,000 tons among some 500 companies.

Of these waste products, the mixed and slightly dirty plastic waste is selected and recycled into bars or poles with polyethylene (by removing the polyvinyl) as the main constituent. About 100 such recycling companies produce about 80,000 tons per year. Polyvinyl films used in agriculture are recycled into fluffs or into a kind of leather.

There are also instances where plastic waste that is not suitable for producing pellets or bars/ poles, laminated composite films (all excluding polyvinyl), wood waste, and cardboard waste are being recycled into solid fuels (in Sapporo, etc.). It is important for both home and industrial plastic waste to be eradicated through recycling, and their energy recovered through their combustion, thereby eradicating plastic waste from landfills. Let us next introduce several models of plastic flow based on some assumptions.

## 8. Plastic Waste and Thermal Decomposition of Plastic Waste/City Garbage

The Association has been conducting thermal decomposition experiments since its establishment. Since then, technical developments have been achieved by many corporations. There are three examples of shaft incinerators employed to dispose of city garbage. The Nippon Steel method is used in the Tochigi machine in Kameishi city, and the Purox method is used in Chichibu city. Meanwhile, the Tsukishima machine employing the Purox method was established in Funabashi city. The machine in Funabashi was not stable in its operation, and was thus declared a failure. Excluding the failures, all attempts are still in their experimental stage, and are not practical yet. Summarizing the processes would look something like the diagram on the following page.

Recently, Fuji Recycling has realized the decomposition of plastic waste with a zeolite catalyst, and a fully operating plant is scheduled to be constructed in Okegawa city.

9. Future Plastic Waste Treatment and Recycling Measures

How products are manufactured and distributed depends on production cost, distribution cost, and consumer taste. When it comes to waste disposal, however, the consumer tends to leave it to the authorities.

In Japan, where landfills are difficult to come by, waste is, as far as possible, incinerated to reduce the volume of those materials requiring dumping. Engineers and the people in charge of these disposal centers are well aware of this problem, and consequently do their best to support the

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Heat
decomposition──┬─┤Plas-├──┬─●Melting bath method
               │ │tic  │  ├─●Two-step method
               │ │waste│  ├─●Pipe steel method
               │ │alone│  ├─●Welding method
               │ └─────┘  ├─●Fluid floor method
               │          ├─●Screw method
               │          └─●Rotary kiln method
      ┌────────┴────────┐
      │Plastic waste mixed│
      │with other garbage │
      └───────────────────┘
          ├── Fluid floor ──┬─●Single tower method (Technical Institute-Hitachi, Ltd.)
          │   method        ├─○Two-tower circumventing method (Technical Institute-
          │                 │                                   Ebara Seisakusho)
          │   Rotary kiln   └─○Byroxu (Tsukishima Kikai)
          ├── method      ────○Landguard (Kawasaki Heavy Industries)
          │
          ├── Shaft method──┬─◐Solution processing method (Nippon Steel)
          │                 ├─◐View locks (Showa Electric)
          │                 ├─◐Track system (Takuma)
          │                 └─◐Combustion device that gasifies through thermal
          │                          decomposition (Hitachi Shipbuilding)
          ├── Retort method────○Test gas process
          │                       (Hitachi Plant, Kanematsu Gosho)
          │
          └── Others       ──┬─●Garrett Process (Mitsubishi Heavy Industries)
                             ├─○Magma-type device (Shin Meiwa Industries)
                             └─○Plasma thermal decomposition processing system
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Legend:
● Oil recycled process
○ Gas recycled process
◐ High temperature melting

Processes for Recycling Plastic Waste

construction of incinerators. However, some academicians and media people do not fully understand the incineration and recycling of plastic waste, and believe that the waste problem can be solved through replacement of plastics with other materials and through the promotion of plastic waste recycling.

At present, research is under way on methods to compare the energy required per unit item consumed per person from the cradle to the grave (excluding the energy recovered from waste incineration) with the status of environmental pollution in the form of air polluting substances, sewage contaminating substances, and the quantity of garbage dumped in landfills. In other words, the energy for all processes from extraction of the resource to production of the raw material to product processing or usage as packaging material to distribution and finally to its disposal as waste. These research efforts have revealed that the material, product shape, or packaging material must be selected with due consideration given to the ecological balance.

According to results of research on ecological balance in the United States and Europe, there is not much difference between paper and plastic products, except that paper has a bigger effect on the environment. In countries with high incinerating ratios like Japan, there are more than three times as many

paper packaging materials, like shopping bags, than polyvinyl products, thus increasing the calorific value and the burden on the incinerators.

The biggest problem with regard to plastic waste from the general household is the reduction of bottles and trays. Detergents are now sold in refillable plastic containers, and this should be promoted. The base cap of PET bottles should be made either of the same PET material or should be made in easy-to-recycle shapes.

The use of plastic trays should be eradicated in some fields. At the same time, packaging replacements like plastic films should be developed. PF activities on the small effects of lightweight trays also would be important.

The actual situation with regard to energy recovery in incinerators is that only about 10-15 percent of the energy recovered is in the form of electrical power, while the rest is in the form of useless water vapor. Many regulations are placed on the incinerators. Assuming that waste cannot be fed into an incinerator when it is not being operated, the energy recovered can be used to supply hot water to the homes in the neighborhood of the incinerator, thereby helping to reduce opposition to the construction of incinerators.

The materials and design for industrial plastic products should be carefully selected so that the product or scrap can be easily recycled at the design or production stage. Product type should also be clearly marked, and measures to promote recycling must be established. Various recycling methods, such as reproduction into pellets, bars or poles, or solid fuels, or even the recovery of energy through incineration after mixture with other waste material must be considered.

In summary:

- Product durability and the reduction or eradication of packaging materials should be planned beginning at the design and production stage.

- Easy-to-recycle products or packaging materials should be planned beginning at the design and production stage.

- Recyclable products and packaging materials should be recycled as far as possible.

- Nonrecyclable products and packaging materials should be incinerated for energy recovery.

— END —

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